NATURAL WEATHERING OF GLASS FIBRE REINFORCED PLASTICS AND DEGRADATION OF THEIR PROPERTIES: AN EXPLORATORY MULTIVARIATE ANALYSIS

by:

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES

(Mechanical Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

April 2019

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Abstract

In this research, different sets of glass/polyester composite material test pieces were used to evaluate the degradation processes induced by natural weathering. Reinforced and unreinforced polyester samples were fabricated and aged in a semi-arid climatic condition in Kelowna, British Columbia, Canada, for all seasons of a year, consisting of a dry/sunny summer, and a cold/cloudy winter. Reinforced composite plates, manufactured under an open-mould hand-layup process, were produced in eight different configurations, varying in their fibre preform architecture, the application of surface coating, and their initial curing state. Unreinforced polyester samples, on the other hand, were only different in their initial curing condition. To study the weathering induced changes in the material properties, not only were the natural degrading agents monitored during the ageing period, but also properties, such as surface hardness, surface roughness, and flexural strength were seasonally measured. Using PCA as an exploratory and multivariate data analysis tool, the correlations were determined between the natural climatic agents and their resultant changes in the material properties. Among the climatic agents, UV radiation, relative humidity, and the depth of snow cover were found as the most affecting agents. The architecture of fibre preform proved to be the most influential factor among the design and processing variables, followed by the surface coating application, and selection of an appropriate initial curing state. Gradual curing in the ambient condition was found to improve the ageing behaviour of GFRP composites, compared to curing at elevated temperatures, as partially cured samples demonstrated less significant sensitivity to photodegradation. Finally, the internal structure of aged samples was morphologically inspected to validate the ageing induced degradation mechanisms. Internal defects, such as weakened interfacial adhesions, cracks along the gel coat interface, and expanded bubbles, were clearly seen in the aged samples using micro-CT inspections.
Lay Summary

Fibre Reinforced Plastic (FRP) composites, as enhanced multi-purpose material systems, have gained wide attention in a variety of applications, ranging from aerospace and marine to construction and power supply industries. The considerable strength and stiffness of these light engineering materials have made them unique alternatives to their metallic counterparts. Despite being beneficial to a myriad of applications, their long-term durability has remained as a grey-area to some designers and has led to the consideration of extremely large design safety factors. Although the outdoor exposure of composites is unavoidable in many applications, the weathering-induced failure may be delayed by the proper selection of the design and processing factors. This research seeks a better understanding of natural ageing and the weathering-induced degradation processes involved in the outdoor climatic exposure of GFRP products. Results have been translated to a preliminary set of recommendations on quality enhancement and the durability prolongation.
Preface

This thesis presents research by Sina Nezafatkhah under the co-supervision of Prof. F. Sassani (Point Grey Campus) and Prof. A.S. Milani (Okanagan Campus). The methodology and the entire data analysis are deemed as an independent work of the author. The experimental tests were obtained by the Composite Research Network (CRN) at the Okanagan Node. A portion of Chapters 3 and 4 have also been accepted for the 11\textsuperscript{th} Canadian-International Conference on Composites (CANCOM), cited as below:


Also, this work was presented at the EGBC (Engineers and Geoscientists British Columbia) research seminar on March 13\textsuperscript{th}, 2019. A version of Chapters 2-4 from this thesis is under submission to peer-journals in the field of composites, material science, and manufacturing.
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<tr>
<td>$E$</td>
<td>noise matrix</td>
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<tr>
<td>$F\ (N)$</td>
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<td>sample thickness</td>
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<td>loading matrix</td>
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<td>$PC_i$</td>
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<td>covariance matrix</td>
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<td>$X$</td>
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<td>$\sigma\ (Mpa)$</td>
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<td>Chopped Samples</td>
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<td>Fully Cured Samples (in-oven cured)</td>
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Acknowledgements

Firstly, I would like to express my highest level of appreciation to my supervisors, Prof. Farrokh Sassani and Prof. Abbas S. Milani. Prof. Sassani was of a tremendous support to me within my career at UBC. He played an influential role in my research and more broadly in my attitude and insight towards life, with his extensive knowledge, his limitless patience, and his most friendly attitude. Prof. Milani broadened my knowledge of composite materials and their manufacturing processes. His support, especially at the early stages of my career, is unforgettable to me.

I would also like to express my sincere gratitude to my examining committee members for the time devoted to reviewing my thesis.

I should pass my special thanks to Mr. Bryn Crawford, Mr. Armin Rashidi, and other members of the Composites Research Network (CRN) Okanagan Laboratory, for their insightful comments and assistance in the logistics around my experimental work. Specifically, I owe my deepest gratitude to Armin, without whose help and effort, the validation of all discussed degradation processes would be undoubtedly impossible. I should also sincerely thank my fellow lab-mates at UBC Vancouver, Mr. Mohammad Ebrahimi, Mr. Masoud Hejazi, Dr. Abbas Hosseini, Dr. Masoud Haghi Kashani, Ms. Hamideh Torabi, and Ms. Sara Azizkhan for all the time we had in the last two years.

Finally and above all, I would like to immensely recognise and appreciate the constant support from my parents who devoted their lives to me and my academic progress, as well as my lovely sister, who supported me both spiritually and financially throughout my MASc studies.
To My Beloved Parents Farhour & Azim

To My Lovely Sister Sadaf
Chapter 1: Background and Thesis Organisation

1.1 Introduction

Application of Glass Fibre Reinforced Polymer (GFRP) composites is widespread in the industry nowadays, ranging from marine operations to construction, and power supply industries. They are widely used in the production of bathtubs, boat hulls, reinforcing rods and tendons, bridge decks, and turbine blades, to name a few. Principally, their considerable strength-to-weight and stiffness-to-weight ratios have made GFRPs an exceptional choice as light materials in a myriad of engineering applications [1, 2].

Despite their benefits, there is a major concern about the long-term durability of GFRP materials under harsh and inconsistent environmental conditions [3]. As an illustration, turbine blades usually encounter extreme climates, particularly in offshore wind farms. Their climatic service condition usually embodies wet/dry periods, high/low-temperature cycles, UV radiation exposure, and even sand erosion. Synergistic effect of these climatic states, besides the impact of reciprocating fatigue loading is reported to be crucial on the long-term performance of composite turbine blades (Figure 1-1) [2].
Indeed, environmental exposure of GFRP composites, and therefore its consequences in degradation of properties (ageing) of pertinent outdoor products, is inevitable in many applications. However, such natural degradation can be limited or controlled by synthesising the initial products under the selection of proper composite constituents and processing parameters. Provision of careful maintenance during the service is also deemed crucial in this regard.

![Weathering-induced failure of a GFRP turbine blade](image)

**Figure 1-1)** The weathering-induced failure of a GFRP turbine blade [4]

To promote reliability on these materials, to significantly boost the quality of products, and to enhance their environmental performance in sensitive applications, not only the mechanisms involved in their natural degradation should be carefully studied, but also a comprehensive analysis on alteration of their properties is deemed to be inescapable. Therefore, a clear trend has been started in the recent literature in studying the engineering aspects of failure for naturally aged composites [2, 3].

### 1.2 Problem Definition and Motivation

To ensure GFRP composites durability under service conditions, as one of the ongoing manufacturers’ concerns, the estimation of their mechanical properties’ degradation is crucial at the product design stage. The scarcity of comprehensive and validated literature data on the
durability of GFRPs is still a major barrier to this estimation. Due to the long experimental time needed, natural climatic ageing is seldom studied; and unlike involved chemical mechanisms, the engineering aspects of ageing-related failures are rarely addressed [5]. Hence, in the absence of reliable ‘longitudinal’ datasets on the ageing performance of GFRP, lack of design knowledge about their degradation mechanisms continues to exacerbate manufacturers’ concerns on GFRP applications under varying environmental conditions [6, 7].

GFRP composites alter in their effective properties under outdoor climatic exposure, either visually or mechanically. This defect, called weathering, has been inveterately neglected by most manufacturers so far and has been offset by consideration of high safety factors, leading to overdesign, enhanced product weight, and material loss [5]. However, considering cost constraints, this cannot be justified nowadays, and a crucial need is perceived by researchers to deepen our knowledge of composites weathering, besides investigating the involved degradation mechanisms.

Lack of knowledge about composites ageing under natural weathering conditions is on the grounds of several reasons. Firstly, ageing is based on a combination of both physical and chemical phenomena, operating at different time scales [8]. Secondly, climatic degrading agents affect each of the composite constituents and the involved interfacial phases differently [9]. In additions, interaction with other ageing processes, such as polymer relaxation [10] and oxidation [11] makes interpretation of composite weathering data rather a complex task.

Also, different climatic regimes lead to different degradation patterns. Indeed, the degradation rate is dependent upon a variety of contributory climatic agents, such as UV irradiation intensity, temperature, and humidity, together with proximity to oxygen [12, 13, 14]. Dimensional stability, besides resistance to both UV and moisture, is considered to be an important durability measure for composites in outdoor applications [13].
UV radiation leads to photo-degradation and chain scission, as for most types of polymers, bonds dissociation energy lies in the range of UV photons energy [15, 16]. Photo-degradation affects composites performance, either mechanically or aesthetically. The decline in both strength and stiffness, besides weight loss, are some of the well-known mechanical side-effects of extended exposure of FRPs to UV radiation [17, 18]. Inferior surface quality, high density of visible bubbles, and faded colour of exposed composites are some of the aesthetical changes imposed by long-term exposure to UV [19, 20].

Before the outset of photo-degradation, UV exposure results in post-curing of resin, making matrix structure more brittle [17, 18]. As UV mostly impacts the irradiated surface, post-curing is mainly concentrated on the outer layers, imposing minimal changes to laminate mechanical properties. Hence, UV radiation effects are deemed mostly visual rather than mechanical [17].

Apart from UV irradiation, moist and humid conditions also cause a decline in both mechanical and visual performance. Water may be absorbed by available polar groups in the molecular structure of the matrix [21, 22], may disperse through matrix void spaces [23, 24], or may diffuse either through fibres [21] or across cracks generated at fibre-matrix interface regions [25, 26]. Therefore, there are various mechanisms involved in composites moisture uptake, each adding an uncertainty source to the selection of pertinent manufacturing processes and leading to a more complex composite design procedure.

Exposure to humid conditions may lead to deterioration of surface quality. Both matrix and fibres may swell under moisture ingestion. Matrix swelling may leave material with blister symptoms on its surface. Additionally, swelling of constituents may result in delamination of laminate layers and therefore inferior surface quality [20, 27, 28].
From a mechanical point of view, moisture firstly softens the resin structure through a phenomenon known as ‘matrix plasticisation’. Fibres, more specifically natural fibres, may also impart moisture ingestion to the material system, even though their original role is to bring additional strength [27]. Diffused moisture, either through or along fibres (along their interface), weakens fibre-matrix bonding, arising poor efficiency in transferring stress to the reinforcements [29], and accordingly a decline in both mechanical and thermal properties [23, 30, 2]. Despite several treatments on fibres to improve their bonding to the surrounding matrix, fibre-matrix debonding has been evidently reported under natural ageing [27].

A few past studies have focused on the derivation of numerical models for the weathering of composites. More specifically using finite element methods, the uptake of moisture and oxygen has been well-addressed for FRP materials [31, 32], providing a better understanding of the involved ageing mechanisms, and thereby helping to improve the design procedure of FRPs. However, numerical modelling of some structural defects, such as imperfections existing in fibres, cracks initiating in the matrix structure, and the void content contained in the material, may be a challenging task. Both analytical and numerical methods, therefore, have broadly failed to model the extreme levels of uncertainty sources existing in FRP composites.

Additionally, among the experimental studies in this area, very few have been performed on the synergistic (concurrent) effect of several destructive ageing agents [33]. This combined interaction of climatic agents is known to impose more serious effects on the material performance rather than their individual impact [1, 3]. As these interactions take place in a variety of modes in real-life scenarios, they are not well understood and are hard to predict [1, 3, 34, 35].

To simulate long-term natural outdoor exposure of composites, a number of studies were provided in an artificial ageing chamber and in controlled condition [36, 37, 14]. Ageing cycles,
however, have been regular and predictable in weathering chambers. The intensity of climatic agents in artificial ageing is also not necessarily the same as those under a natural ageing condition. Thus, no precise correlations may exist between artificial and natural ageing research results [38, 1].

As a result, a comprehensive ‘longitudinal’ analysis of naturally aged composites, especially GFRP composites, is deemed necessary in the literature to find better design and manufacturing conditions for enhanced weathering performance of these widely used materials. In particular, an integrated experimental-multivariate statistical analysis can be helpful to correlate the ‘observed property degradations’ to the contributory ‘natural weathering agents’ along with the ‘material and manufacturing decisions’ made at the stage of fabricating the composite products.

1.3 Research Objectives

Unlike most of the studies in the GFRP weathering area, this research is carried out under natural and uncontrolled outdoor exposure through a longitudinal experimental design. As a general objective, variations in select GFRP composite properties will be studied under the synergistic interactions of diversified natural agents. To arrive at practical recommendations on quality enhancement and durability prolongation of the GFRPs, the effect of select manufacturing conditions as well as material design factors have also been included in the analysis.

More specifically, the specific objectives of the study are as follows:

- Study the natural ageing effects of miscellaneous climatic agents on GFRPs performance, either visual or mechanical. This is fulfilled by implementing a Principal Component Analysis (PCA) as an effective multivariate data analysis technique.
- Identify the involved degradation mechanisms and estimate their causes.
• Make recommendations on the initial curing condition as well as the choice of fibre architecture to enhance GFRPs quality by prolonging their environmental durability.

1.4 Thesis Outline

The thesis started in the current chapter with a general introduction to the degradation of GFRP composites under natural climatic exposure (Chapter 1), followed by research motivations and objectives. An extensive literature review will be presented in Chapter 2, where some earlier studies in the field are discussed and compared. Then, in Chapter 3, The methodologies used for GFRP weathering property measurements and data analysis (PCA) are presented. Results are discussed in Chapter 4 together with some suggestions on manufacturing and design decision factors. Finally, in Chapter 5, the main conclusions of the work are drawn, and directions to potential future works are outlined.
Chapter 2: Literature Review

2.1 Effect of Water/Moisture Uptake and Corrosive Media

2.1.1 Effect of Tap/Deionised Water

Polymer composites are prone to moisture ingress in a humid atmosphere and when immersed under water [27]. Prolonged moisture ingress may cause composites to lose their properties and functionality. Moisture uptake in composites is dependent upon several factors, such as temperature, fibre volume fraction, reinforcements type and orientation, permeability nature of fibres, exposed surface area, diffusivity, the reaction between water and matrix, and finally the application of surface protection agents [27]. These moisture uptake repercussions are summarised in Figure 2-1.

![Figure 2-1) The main effects of moisture absorption in composites](image-url)
Effect of fibre alignment in moisture uptake was investigated in [39]. More potential for moisture ingestion was detected for composites with symmetrically aligned fibres than their asymmetrically aligned counterparts, and the degradation of properties was more intense in the former.

By applying gel coat, as a frontline surface protection and short-term solution [27], composites may experience less moisture ingestion and fewer microcracks; however, additional interface regions, imposed by veils and coatings, may result in moisture uptake [40]. Accordingly, crack propagation at interface regions is probable and the applied coating may peel from the bulk of the material system. Therefore, the invasion of moisture to the resultant free volume may impose degradation (Figure 2-2).

![Image of gel coat peeling from GFRP material]

**Figure 2-2) Peeling of gel coat from the bulk of a GFRP material**

Moisture diffusion in polymers is also dependent on other factors, such as polarity of the matrix, the extent of crystallinity for resin (in thermoplastic resins), and finally existence of any other water attracting agents, like residual hardeners and crosslinking agents [21, 22]. Resins with more polarity in their molecular structure have more moisture ingression potential, as polar groups are inherently moisture absorbent. Pigments added to resin are also known to increase the risk of
moisture sorption. Besides, most of the materials used as crosslinking agents and hardeners are moisture absorbent, and therefore their residual in matrix structure enhances moisture ingestion.

Water uptake behaviour is more predictable and well documented in the literature for shorter exposure times; however, for prolonged exposures, other effects, such as, fibre-matrix interface cracking [41], material leaching [42], and polymer relaxation [43] play a role, adding more uncertainty sources to the material system and complexity to their design process.

A general behaviour observed for moisture ingress at room temperature is called Fickian. This trend starts with a linear increase of absorbed water against the square root of time at the first stages, before the outset of saturation, when the moisture absorption rate dramatically slows down [44], as shown in Figure 2-3.

![Figure 2-3) Fickian behaviour for moisture absorption](image)

Moisture uptake is accelerated at elevated temperatures [1, 45, 46]. Indeed, the higher density of micro cracks in composites at elevated temperatures and their higher void content means their higher permeability. The decreased viscosity of water at higher temperature, together with the
imposed thermal gradient to the material, also facilitates water penetration and therefore intensifies the risk of moisture sorption [21, 47, 48, 49, 50].

Moisture ingression mainly follows Fickian law for neat resin, although deviations have been reported in the literature [2, 9, 43, 51]. These deviations are mainly attributed to resin relaxation [43] and hydrolytic chemical reactions [52]. However, in composites, although the Fickian trend can be initially detected, significant deviations are often observed after longer exposure times [2, 51, 53, 54, 55]. According to Rocha et al.’s results [2], moisture uptake ratio rises in composites after long-term immersion. Moisture sorption in composites is composed of two phases. The first phase follows the Fickian law until saturation, and the second phase continues with more uptake ratio compared to the Fickian behaviour (Figure 2-4). The second phase, arising after saturation, is mainly due to the promotion of free volume caused by topological changes in the material microstructure, such as microcracks formation and fibre-matrix debonding [42].

![Figure 2-4) Different phases of moisture ingression in composites](image)

Moisture sorption in composites is through the combined action of diffusion in matrix and capillarity along fibres (either diffusion through fibres, broadly reported for natural fibres, or cracks at fibre-matrix interface region, stated for both natural and synthetic reinforcements in the
Composites are proven to be more diffusive along their fibres [17, 56]. During diffusion through matrix medium, some water molecules are attached by hydrogen bonds to hydrophilic groups in the matrix, while others fill the free volume in the polymeric network. Generally, moisture uptake is enhanced by the further development of cracks, as water fills the newly developed empty spaces [24, 57].

Mechanical tests have implied that combined ageing effects such as matrix plasticisation or resin softening [9] and weakened fibre-matrix bonding [52, 58, 59], all dominating both resin and interfacial regions, can lead to degradation of effective mechanical properties [53]. Moreover, swelling of both fibres and matrix, together with delamination of layers, can lead to surface roughening [20, 28] and deteriorates the composite surface quality.

### 2.1.1.1 Imposed Changes on Matrix Structure

Absorbed water molecules may cause resin softening through a phenomenon known as ‘plasticisation’. In this phenomenon, water molecules, penetrated between polymeric chains in matrix molecular structure (Figure 2-5-a), act as a lubricant and facilitate chains mobility (Figure 2-5-b). Plasticisation imposes drop in the glass transition temperature ($T_g$) [53, 54] and has been detected to be reversible after desorption [2, 37].

![Figure 2-5](image_url) Plasticisation effect; water molecules act as a lubricant and facilitate the mobility of chains (a)

Penetration of water between polymeric chains (b) higher mobility of chains after saturation

Another effect of absorbed moisture is the chemical interaction of water molecules with polymeric chains, known as ‘hydrolysis reaction’ (Figure 2-6). Hydrolysis reaction results in
chains scission and leaves the matrix molecular structure with chains of lower length and therefore of lower intermolecular Van der Waals bonds. Given the dwindled intermolecular forces between scissed chains, these reactions are generally followed by the leaching of the broken chains from the bulk of the material, and ultimately affects the surface quality [53, 60].

\[
\begin{array}{c}
\text{R}_1\text{O}_2\text{R}_2 + \text{H}_2\text{O} \rightleftharpoons \text{R}_1\text{OH} + \text{R}_2\text{OH}
\end{array}
\]

*Figure 2-6) Hydrolysis reaction for polyesters*

Apart from surface quality, the diminished intermolecular bonds between scissed chains mean the degradation of mechanical properties. Hydrolysis reaction may also degrade the bonding of fibres to their surrounding matrix. Dissolution of fibres sizing in water [9], together with fibres corrosion under moisture invasion [61], may even worsen this scenario and lead to ultimate interfacial fibre-matrix debonding. Leaching of composite constituents, namely fibres and matrix, or their interface regions is experimentally confirmed by Rocha et al. [2]. As an important clue to the leaching phenomenon, weight loss was evidenced for aged GFRP samples after undergoing a desorption cycle, compared to their unaged counterparts.

Among the two competing degradation mechanisms in matrix media, namely plasticisation and hydrolysis reaction, the former is the dominant one [2, 62]. Firstly, stress-displacement curves in [2] suggested more ductility of GFRP composites, saturated by water, rather than their dry counterparts. Dry samples were of less ultimate strain, with steeper drop experienced in their load tolerance before ultimate failure. Cracks propagation pattern reported in [2] also confirmed more ductility of soaked composites. After destructive tests, cracks were propagating and then were arrested inside fibre bundles in saturated samples, as opposed to dry composites where cracks
propagation was along fibre bundles. This more ductile failure denoted the dominance of matrix plasticisation over chemical hydrolytic reactions.

Moisture ingression may result in additional hardening after desorption due to pseudo/secondary crosslinking (Figure 2-7-b) [2, 57]. There are two types of bound water in the resin network as follows.

The first type, type I, is of less activation energy and thus removed more easily through the desorption cycle. This type is originated from the formation of single hydrogen bonds between one polymeric chain and diffused water molecules (Figure 2-7-a) [57]. Formation of these bonds leads to reduced intermolecular Van der Waals forces, as water molecules fill the free volume between chains. Hence, polymeric chains become more mobile, and accordingly matrix structure softens or plasticises. This type of bound water also yields to matrix swelling, principally because of more volume occupied by water molecules.

![Figure 2-7](image)

*Figure 2-7) Different types of hydrogen bonds formed in the epoxy network: (a) a single hydrogen bond formed between a water molecule and a polymeric chain, (b) multisite interconnective hydrogen bonds formed by water molecules, bridging between the polymeric chains [57]*
On the other hand, type II bound water, with more activation energy, is the product of a multi-site interconnective hydrogen bonding model (Figure 2-7-b). This type of bound water, known as a pseudo/secondary crosslinking, bridges between two polymeric chain segments, and accordingly leads to reduced chain mobility in the polymeric network (Figure 2-7-b) [57]. Although widely discussed in the literature for epoxy resins, pseudo crosslinking is also reported for polyesters [63, 64]. Indeed, in polyester resins, a water molecule can attach through hydrogen bonds to either hydroxyl groups (−\(\text{OH}\)) at the end of polymeric chains or carbonyl groups (\(\text{C} = \text{O}\)) along chains length [37] and accordingly bridge between two chains. Amount of type II bound water is proven to increase by exposure time and temperature [2].

Formation of type II bound water was also experimentally confirmed by Rocha et al. [2]. Firstly, the residual weight in the un-reinforced samples dried after their saturation, was a meaningful clue to type II bound water molecules. This residual weight was revealing the presence of water molecules, more strongly bound to the resin network compared to their type I counterparts and accordingly needing more energy for desorption. Secondly, compared to unaged unreinforced samples, neat resin specimens increased in their glass transition temperature (\(T_g\)) when dried after their saturation. Failure mode also shifted to brittle failure, which was additional evidence for the formation of type II bonds [2]. Brittleness of dried neat resin samples may also be attributed to another phenomenon, known as polymer relaxation. Indeed, free volume in resin molecular structure modifies after removal of absorbed water molecules, leading to relaxation of resin [43].

2.1.1.2 Imposed Changes on Fibre-Matrix Interface Regions

Weakened bonds between fibres and their surrounding matrix or their ultimate debonding may be another outcome of moisture sorption in composites. These are reported as the dominant damages among those that moisture ingestion may impose on GFRP composites [2, 26].
Weakened interfacial bonds are the result of both matrix plasticisation and chemical hydrolysis reactions [26, 65, 66, 67, 68, 69] and affect thermomechanical properties [19, 20, 70, 71, 72], mainly bending strength.

Attenuated interfacial bonds under the invasion of moisture have been experimentally witnessed by Rocha et al. [2]. Cracks were propagating along fibre bundles in aged GFRP samples after destructive tests and were not affecting the surrounding resin. This clean debonding palpably signified degradation at interfacial bonds in the saturated samples. Additionally, mechanical properties in GFRP composites had degraded more when saturated, compared to their neat resin counterparts. This more degradation further reinforced the hypothesis that the fibre-matrix interface is notably affected by moisture uptake.

Particularly, the combined effects of differential swelling stresses [58], chemical hydrolytic reactions [60], matrix plasticisation [54], fibre corrosion [61] and dissolution of fibres sizing [9] lead to the ultimate fibre-matrix debonding. Generally, debonding promotes capillarity in the material structure, as moisture may invade the resultant free volume [2]. Based on the chemical composition of fibres, two different mechanisms may be involved in this debonding, as described below.

![Figure 2-8](image)

(a) Before saturation  
(b) After saturation

Figure 2-8) Different swelling rates between the hydrophobic fibres (represented by black lines) and a typical polymeric matrix (shown as the yellow area), leading to their ultimate debonding
In composites reinforced with hydrophobic fibres, such as glass fibres, the absorbed water (under extreme exposure conditions) causes swelling in the matrix, while rarely do these types of fibres swell owing to their negligible water uptake. Different swelling rates between fibres and matrix result in internal stresses (Figure 2-8) and crack formation. Generated cracks may propagate more easily along corroded interfacial phases, eventually leading to interfacial debonding [2, 58].

On the other hand, in composites with hydrophilic reinforcements, such as natural fibres, debonding mechanism is slightly different. These types of fibres have a reputation for significant swelling under moisture ingression. Principally, water molecules may establish intermolecular hydrogen bonds with hydrophilic groups in their chemical composition, resulting in their swelling. Cracks may form and propagate in the corroded interface region around fibres, as swollen fibres impose stress on their surroundings. Finally, leaching of water-soluble substances from fibres further aggravates this scenario and leads to ultimate debonding [23, 27].

The interfacial debonding was visually spotted in [2]. Opposed to unaged GFRP samples, fibre bundles were visibly traceable in their saturated counterparts. Visually detectable fibre bundles in aged samples were representative of cracks propagating along fibres and their debonding from the surrounding matrix.

Some moisture-induced damages, such as material leaching [2, 73, 74], microcracking, and interfacial debonding, are known to be irreversible [2]. On the other hand, plasticisation and differential swelling stresses are fully recoverable after desorption, together with hydrolysis reaction as a partially recoverable degradation process [2, 37]. Presence of hydroxylic groups in fibres sizing may slightly mitigate fibre-matrix debonding [37, 75, 76, 77]. Namely, intermolecular hydrogen bonds may form between these hydroxylic groups and matrix polymeric chains.
Therefore, water molecules, bridging fibres to the matrix, may promote some extent of reversibility to debonding.

2.1.2 **Effect of Sea Water and Corrosive Media**

Under immersion in seawater, the degradations of GFRP composites have been reported to be generally the same as those for deionised water [53, 39].

An artificial solution was used in some experiments as representative of sea water. Fang et al. [53] used an artificial solution and found it less damaging than tap water. The salt solution is of more molecular weight and more density; therefore, its flow is restricted. Also, salt crystals may penetrate to the material structure and impose additional hindrance to penetration of destructive water molecules [53, 78, 79].

Natural seawater, on the other hand, is reported by Aldajah et al. [39] as a media with more damaging effects on GFRP composites, compared to tap water. Effect of natural seawater is mainly dependant upon its chemical composition and should be varying from place to place. This more degradation by natural seawater should be based on its more alkalinity compared to the typical tap water [80]. In a study carried out by Bazli et al. [80], alkaline media was reported as the most destructive environment to GFRP composites, compared to both acidic and seawater media, which were ranked consecutively the next.

Immersion under natural seawater more dramatically affects the surface quality [81]. Indeed, sodium hydroxide may form under reaction between sodium ions from seawater and hydroxyl groups in polymeric chains. The resultant pressure from this formation causes some blisters on the surface of submerged GFRP composite and affects the surface quality.
2.2 Ultraviolet (UV) Irradiation and Photodegradation Effects

Ultraviolet (UV) radiation also has adverse effects on composites, more specifically on their matrix structure. More damages are usually expected by UV radiation rather than exposure to elevated temperature. As an example, more changes in composites were detected in [17] under UV radiation rather than thermo-oxidative media.

Although stiffening and modifying the matrix structure under moderate exposure times, extended UV radiation can trigger photodegradation or photooxidation in the proximity of oxygen [25]. Fleeting period of UV irradiation normally has minor effects [82]. However, prolonged exposures contribute to changes in molecular structure (in both monomer units and polymeric chains) [37], in the appearance of composites (their colour and glossiness) [83], and in their mechanical properties [17]. UV radiation effects are summarised in Figure 2-9.

Figure 2-9) Main effects of UV irradiation on composites

The flow of oxygen and the resultant effects were investigated under UV irradiation, in a study by Liau and Tseng [84]. More degradation was evidenced for composites under synergistic
exposure to both UV radiation and airflow, rather than those irradiated in a vacuum. Broken chains in the latter case were not capped by external molecules and hence re-bonded again.

UV radiation may accelerate oxidation as a destructive reaction [82]. Degradation inflicted by UV is mainly limited to the vicinity of the irradiated surface [25]. Indeed, outlying layers protect internal sections from degradation, as they consume diffused oxygen and retard UV rays.

The UV radiation is also reported to slightly mitigate the moisture ingression repercussions [5]. Irradiated surface starts to shrink, as cross-linking actions make matrix structure more compact (exaggerated in Figure 2-10). The resistance of protected unexposed layers against this shrinkage leads to the imposition of internal compressive stress (Figure 2-10-b), promoting fibre-matrix bonding and alleviating matrix swelling. Therefore, minor mitigation of moisture sorption side-effects is plausible by exposure to UV radiation.

![Figure 2-10](image.png)

(a) Before irradiation  
(b) After irradiation

Figure 2-10) Shrinkage of the UV irradiated surface, improving the interfacial bonds (black lines represent fibres and the yellow area shows the surrounding matrix)

Studies on UV radiation and the resultant photo-degradation are developed by either complex structural analysis techniques or data analysis methods [83, 85, 86, 87, 88]. Scanning Probe Microscopy (SPM) and Fourier Transform Infrared Spectroscopy (FTIR) are the popular structural analysis techniques in the literature to evidence changes in atomic scale. Data analysis techniques
are commonly applied to measured mechanical properties to assess how the material performance is shifting due to exposure conditions.

2.2.1 **Imposed Changes in Molecular Structure**

In the molecular scale, UV radiation may ultimately lead to chains scission after long exposure times. For instance, in polyesters, the dissociation energy of $C-O$ bonds in ester groups corresponds to wavelength from 315 nm to 400 nm. This dissociation energy falls within UV-A rays, barely filtered by the ozone layer in the stratosphere. Hence, chain scission in polyesters is more probable from $C-O$ bonds under natural climatic exposure [82]. Chains breakage from $C-C$ bonds in the matrix molecular structure is also reported in the literature [16, 37, 89, 90].

Apart from matrix degradation, reinforcements may similarly corrode by exposure to UV [82]. As an illustration, oxide groups contained in glass fibres, such as $Si-O$, $Al-O$, and $Mg-O$, are also in risk of bond breakage under natural UV radiation. The resultant free radicals may impose further degradation and chain scission to the material structure.

Scissed chains with lower molecular weight and accordingly dwindled intermolecular Van der Waals bonds are more susceptible to be leached from the bulk of the material. This leaching from the bulk of resin affects surface quality and leads to an excessive roughness on the irradiated surface [83]. Removal of broken chains is evidenced by Wang et al. [17]. For GFRP composites aged under UV radiation, exposure of reinforcements was a significant clue to leaching of broken chains from the external layers.

Photo-thermal oxidation and the resultant bonds scission may also increase polarity in the matrix structure and accordingly raise the potential for moisture sorption [83]. Polar groups, such as alcohols and hydroperoxides [37], may form after chain scission. Owing to the potential of these
groups in developing intermolecular hydrogen bonds with water molecules, the risk of moisture ingress is enhanced.

Before the outset of photo-degradation, UV radiation leads to a firmer structure of the matrix, typically on the irradiated surface [16, 17, 89, 90]. Chains including remained unsaturation in their chemical structure (\( c = c \) bonds) may crosslink to each other under the action of UV radiation. This phenomenon, known as post-curing, leads to additional consolidation, and accordingly more solid structure of the matrix molecular arrangement.

Also, unreacted monomers may polymerise by UV, a reaction known as esterification for polyester resins. Polymerisation ultimately strengthens intermolecular Van der Waals bonds, as it leads to increased chain length and accordingly more molecular weight in the matrix structure. Indeed, the combined action of both post-curing and polymerisation leads to a more compact structure in the matrix before the start of photo-degradation [16, 17, 89, 90].

These effects were experimentally evidenced by Wang et al. [17], using FTIR spectroscopy. Drop and rise, evidenced consecutively in the density of hydroxyl groups (\(-OH\)) and methane groups (\(-CH_2-\)), signified chain lengthening or polymerisation in the middle stages of ageing by UV radiation. In addition, a drop in the density of alkene groups (\(-C = C-\)) in aged samples was a sign for post-curing and cross-linking.

### 2.2.2 Cracks Formation

UV radiation also leads to the evolution of slight density gradients and subsequently residual stress in composites, ultimately precipitating cracks formation in their structure. Photo-degradation and the resultant chain scission leaves composites with lower density on their outer layers. On the other hand, both post-curing and polymerisation, as short-term UV exposure outcomes, lead to a
denser and more compact structure at the irradiated surface. The consequent residual stress in the material, either after short or extended exposure to UV, results in internal stress and ultimately generation of microcracks in the material structure [13, 36].

Diurnal temperature variation is another contributory climatic factor in cracks formation [84]. Considering differences in the coefficient of thermal expansion (CTE) between fibres and matrix, daily variations in temperature can impose internal thermal stress (residual stress) and eventually form cracks. Generated cracks are additional pathways to invasive oxygen and therefore contribute to further aggravation of matrix erosion [5].

2.2.3 Imposed Changes in Performance of Composites

Firstly, GFRP composites change in their visual performance by UV radiation and the resultant photo-degradation. UV affects surface quality and alters both colour and glossiness of these materials [17, 83, 91]. Evident bubbles formed by the photochemical changes in the matrix structure [82] may also affect visual as well as mechanical performances.

Delamination of reinforced layers was verified for irradiated GFRP composites by Croitoru et al. [83], where the material surface roughness was more intense after irradiation. Namely, leaching of broken polymeric chains from the bulk of the material led to inferior surface quality of samples after prolonged exposure to radiation. Significant colour changes were also evidenced in [83] for composites aged under UV irradiation. Chromophoric groups, such as groups containing $O - H$ and $C = O$, may form after photo-oxidation, yielding to darkening of samples [83].

Photo-degradation is also affecting glossiness in GFRP composites. In the matrix structure, the presence of metallic ions, like cobalt ions, may further deteriorate this loss of glossiness [17]. These metallic ions, typically used as promoters, take part in chemical reactions and hasten chains
scission in the matrix molecular structure. Inorganic fillers, such as $Al(OH)_3$, are also detrimental to both surface quality and appearance of composites. Indeed, these fillers degrade after UV radiation and release free radicals. The resultant free radicals contribute to chain scission and further erosion of matrix structure [17].

Apart from their visual performance, mechanical properties may also be affected by UV radiation. However, their changes are proven to be minor since only a thin layer, adjacent to the irradiated surface, is affected [82]. Both tensile and bending strengths were evidenced to be rising at the first stages of radiation, followed by their decline after prolonged ageing [17]. The initial rise was attributed to the combined effect of polymerisation and post-curing, while the subsequent decline is the photodegradation aftermath. Formation of microcracks after UV radiation, together with debonding of fibres from the surrounding matrix, may also lead to additional degradation of mechanical properties. As a clue to debonding induced by UV radiation, fibre pullout was evidenced by Gu [82] after the failure of GFRP samples and mainly around their irradiated surface.

More fibre content in composites generally implies an improved ageing resistance and better properties retention [82]. As an important clue, fibre reinforcements were identified in [5] to defer ageing discolouration for GFRP composites. Firstly, fibres bind the matrix structure and therefore hinder its degradation [5]. Secondly, photochemical reactions are delayed when composites contain more fibre content, as fibres impede the penetration of UV rays into the material’s internal sections [91].

Coating application is also known to be effective for composites to limit their erosion under UV radiation [83]. Veils and coatings absorb UV rays and impede their entrance to the body of the composite material. However, coatings are also themselves permeable and often transparent to some ranges of UV wavelength spectrum. The colour of the applied gel coat also plays a significant
role. As an illustration, white coatings were evidenced in [83] to be more transparent to UV rays compared to their red counterparts and more damages were detected in samples with a white gel coat on their surface.

2.3 Accelerated Weathering

Although the individual impact of each climatic agent on composites weathering is well studied in the literature, studies targeting their synergistic (combinative) effect are scarce [33]. To meet this objective and to assess composites long-term environmental performance, numerous studies have aimed at artificial ageing experiments. Particularly, the reproducibility and swiftness of these controlled ageing experiments [14, 36] have made them popular among researchers, as a convenient method.

In artificial ageing, natural climatic exposures are simulated by an ageing chamber under a controlled condition. Composites undergo cyclic exposure to UV radiation, moisture, and heat in ageing chambers. To precipitate degradation, accelerated ageing experiments are generally carried out at elevated temperature. Performance of composites is monitored in predefined intervals, and their changes are evaluated in different conditions [27].

Both reinforced and un-reinforced isophthalic polyester resin samples have been artificially aged in a study by Mouzakis et al. [37]. Composites were reinforced with glass fibres, while other samples were neat resin specimens. Ageing was carried out at an elevated temperature in an ageing chamber, under cyclic exposure to UV radiation and humidity. Post-curing (discussed in Section 2.2.1) and pseudo crosslinking (discussed in Sections 2.1.1.1 and 2.2.1) notably led to the stiffening of un-reinforced samples. However, for reinforced composites, no strong results were derived, chiefly because of inaccuracies crept into experiments. As an illustration, differences
between the dimensions of reinforced and unreinforced samples were clear sources of error in this study.

The durability of pultruded E-glass fibre reinforced polymers (E-GFRP) was studied in [1]. Provided samples, synthesised from three different types of resin, namely isophthalic polyester, orthophthalic polyester, and vinyl ester, were artificially aged in an ageing chamber. Ageing comprised extreme conditions, such as high temperatures, freeze-thaw cycles, moisture, and UV radiation. All samples were monthly declining in their both mechanical and visual performance after six months of ageing. The lower level of moisture ingestion was evidenced for samples with vinyl ester resins, implying their hydrolytic stability compared to the other two counterparts. Less variation in mechanical properties during ageing in this type also implied their more degradation resistance.

Among measured properties in [1], namely either flexural or tensile strength and stiffness, flexural strength was evidenced as the most sensitive property to ageing. Indeed, samples were shifting in their flexural strength more dramatically during ageing, compared to other measured properties.

Synergistic effect of climatic agents was investigated on E-glass and ECR-glass-based composites in [33]. Ageing was carried out at an elevated temperature in an ageing chamber, whose environment was comprised of UV radiation and water condensation. The weight of samples was monitored during the ageing span; similarly, surface quality was inspected, yet only at the end of ageing. Stronger and more extensive erosion was evidenced under the combined action of climatic agents rather than their individual influence. This was firstly for the formation of hydroperoxides, and secondly owing to the removal of water soluble and insoluble particles.
Hydroperoxides, formed under synergistic exposure to UV radiation and moisture, are highly reactive intermediates and contribute to scission of unaffected polymeric chains [92, 93]. Decreased intermolecular forces between broken chains firstly suggest their potential to be removed from the material bulk and secondly implies a decline in mechanical performance. The former material leaching from the surface leaves inner layers unprotected and therefore in risk of damage and further degradation.

The durability of composites reinforced by chopped (short) glass fibres was investigated in [5] at elevated temperature and under exposure to UV radiation and moisture. Test specimens were composed of mixed Plastic Solid Waste (PSW) with reinforcement weight fraction varying from 10% to 30%. Comparison of results with neat unreinforced PSW samples revealed more property retention for reinforced specimens. More fibre content in samples was boosting their property retention during ageing.

Particularly, fibres hindered additional degradation in this experiment, as they hold the resin chunk and hamper cracks formation. Also, considering the discontinuity of fibres, fibre-matrix debonding was not a paramount issue in this case. Overall, in composites with chopped reinforcements, higher fibre content led to less moisture ingress and accordingly more retention of properties. Results also suggested UV radiation as a mitigating agent on moisture ingress side-effects such as matrix swelling and weakened fibre matrix bonds. Namely, shrinkage of irradiated layers is inhibited by unexposed internal sections; and hence the resultant compressive stress can lead to improvement of fibre-matrix bonding (Section 2.2).

Pultruded E-glass fibre reinforced polymer (E-GFRP) bars were provided in four different diameters in [3] and were artificially aged at elevated temperature. All samples were composed of epoxy resin as a matrix and aged in an ageing chamber, under sequential exposure to UV radiation
and water vapour condensation. The impact of each degrading agent was investigated on all types of bars at different stages. To explore the effect of weathering factors, mechanical properties were monitored during the ageing period. The gathered data was subsequently analysed to explore the significance of each effect.

Morphologically, microcracks caused by differential density stresses (discussed in Section 2.2.2) were deemed as a major concern in [3]. Cracks, mainly formed by UV radiation, were evident on the surface of bars aged for 3000 hours. Among agents involved in moisture ingression, the effect of relative humidity was more detrimental than water immersion, as water molecules are more mobile in gaseous status. Even though a general decline was evidenced for flexural performance, ageing did not impose significant changes on tensile properties. Indeed, tensile performance is more strongly related to fibre properties, which are not dramatically affected by climatic ageing. Variations in tensile properties were detected only when the surrounding temperature was reaching $T_g$ (95°C for the epoxy resin), with a more dramatic decline when it surpassed this threshold (dramatic decline triggered at 200°C for test specimens).

Analysis of Variance (ANOVA) was the statistical analysis method adopted in [3]. Statistical analysis revealed the significant influence of both exposure time and the sample’s diameter on shifts in mechanical properties. Primarily, exposed layers of the material are vulnerably under the threat of climatic agents rather than their core, with even more intensified degradation at prolonged exposures. Thus, the risk of ageing induced decline in mechanical properties was deemed to be higher for bars with smaller diameters and extended ageing period in this study.

The limited number of measurements carried out at each exposure stage in [3] (3 samples for each test) may not ensure the normality of data, while the normal distribution of residuals is one
of the main requirements for ANOVA; accordingly, some errors in interpretation of ANOVA results may be expected.

2.4 Natural Weathering

While the speed of experiments in accelerated ageing tests has convinced many researchers to use artificial ageing chambers in material weathering studies, there are reports showing no exact correlations between artificial and natural ageing scenarios [38], especially regarding mechanical properties degradation [1, 5].

Ageing cycles are regular and predictable in ageing chambers, as opposed to unpredictable and ‘chaotic’ cycles that parts may experience in real (natural) weather conditions [38]. Primarily, the rate of composite degradation is dependant upon several factors, such as UV radiation, temperature, humidity, precipitation, and their intensity [12]. Differences in the severity of climatic agents may change the involved degradation process, as different weathering regimes result in different degradation patterns [13]. Hence, a deep insight into the natural weathering of composite parts may not be ensured by artificial ageing experiments.

Natural ageing has scarcely been addressed in the literature, as significant time and effort is required for such tests [27]. These experiments are mostly performed in the exposure to a climate in which the eventual product is expected to be during its service [38]. Long-term performance of specimens is typically monitored by real-time measurements during the ageing period [25].

Natural durability of pultruded E-glass fibre reinforced polymers (E-GFRP) was studied by Sousa et al. [6]. Test specimens, all of which were composed of either polyester or vinyl ester resin as a matrix, were subjected to either accelerated or natural ageing. As was expected, vinyl ester
samples presented more stability in their properties during the experiment, compared to their polyester counterparts, and accordingly more resistance against ageing.

All samples, aged in either condition, were significantly altering in their visual performance, such as their surface colour and glossiness. Fibre blooming was an additional concern after ageing in both scenarios, affecting surface quality. Photochemical degradation and the subsequent leaching of degraded segments notably led to unveiled exposure of glass fibres.

Comparison of both ageing conditions revealed a strong correlation between artificial and natural ageing in the visual appearance of aged samples. However, among the measured mechanical properties, such a correlation was not so strong for tensile strength. Indeed, samples were consistently declining in their tensile strength when aged artificially, while fluctuation was evidenced for this property during natural ageing.

The discussed study [6] could not address the effect of seasonal climatic changes on composites performance, as measurement increments were so wide (10 months) for the natural ageing experiment. Also, the effect of each climatic degrading agent, namely temperature, UV radiation, humidity, and precipitation, was not precisely studied as an exploratory multivariate analysis.

Carra and Carvelli [1] also studied the natural ageing of pultruded E-glass fibre reinforced polymer (E-GFRP) composites and detected variations in their both mechanical and aesthetical performances. Comparison of results with those in artificial ageing revealed no meaningful correlations between the two ageing conditions. Notably, differences between artificial and natural weathering cycles led to this contradiction between the results. As an illustration, the two ageing scenarios are not necessarily the same in the wavelength of the involved UV rays or the intensity of other degrading agents. In this study [1], variations in properties were not diligently monitored.
during the natural ageing period. Measurements were only involved at the end of the one-year span of natural ageing without monitoring properties during the natural climatic exposure.

2.5 Summary

In this chapter, a number of earlier studies on GFRPs degradation were reviewed. Incurred changes under the climatic exposures, both under artificial and natural ageing, could be justified via the following factors:

- Moist and humid environments notably diminish composites strength and stiffness. The main outcomes of moisture ingression were found to be matrix plasticisation, swelling of both fibres and matrix, broken polymer chains under hydrolysis reactions, weakening of fibre-matrix bonds and eventually their debonding, and finally matrix hardening after desorption (pseudo-crosslinking)

- UV irradiation is generally involved in photo-degradation and microcracks formation. Changes inflicted by UV radiation are typically evidenced in composites appearance rather than their mechanical performance.

Even though degradation is found to be significant under the synergistic interaction of climatic agents, studies reporting composites natural weathering are seen to be very infrequent, with minor emphasis on the effect of seasonal changes, plus the impact of the manufacturing process and design variables. Namely, the role of variables such as reinforcement architecture type, gel coat application, and the initial curing process have been neglected in the pertinent literature. Also, a multivariate exploratory data analysis is deemed to be essential to more reliably study the impact of climatic agents, as the composite is exposed to the synergistic interactions of numerous ‘uncontrolled’ factors under natural weathering. This, in parallel to the identification of the effect
of above exemplified ‘controlled’ manufacturing and design factors, can be highly advantageous for durability estimation of GFRP products by composite manufacturers.
Chapter 3: Methodology and Experimental Procedure

3.1 Samples Preparation

In this research, test specimens were fabricated with three major variations in their constituents and processing condition, including fibre preform architecture (continuous E-glass plain weave 400 $g/m^2$ or randomly chopped E-glass fibre mat 800 $g/m^2$), coating application (either treated with Polycor® isophthalic white gel coat on the surface or without this treatment), and the initial curing state (either cured in ambient lab condition or at elevated temperature). All samples were made of Envirez™ unsaturated polyester resin with methyl ethyl ketone peroxide as an initiator in 1.25% of resin weight. Along with unreinforced neat resin test specimens, reinforced samples were provided at approximately 35% and 40% of fibre volume fraction for randomly chopped mat and continuous plain weave laminates, respectively.

All samples were fabricated through conventional open mould hand lay-up process, with laminate stacks consisting of 6 and 25 plies, respectively, for chopped mat and woven fabric laminates. The curing process was carried out on a flat sheet of stainless steel 304 alloy as tooling, under two different processing scenarios, either in ambient lab condition or at elevated temperature using an industrial oven. Ambiently cured test specimens were cured slowly in a controlled environment at 21°C and 33% of relative humidity for approximately one day, whereas other
samples were cured swiftly in an oven at 50℃ for a minimum of 6 hours. The initial degree of cure (DOC) was estimated using RAVEN, a cure modelling software, as roughly 84% and 96% for ambiently and in-oven cured samples, respectively. After curing, provided samples were cut into smaller pieces using an abrasive waterjet cutting Omega 2652 JetMachining Centre. The final dimensions (13 mm × 215 mm) were in accordance with ASTM D7264/D7264M standard for 3-point flexural bending strength testing (3PB test) for polymer matrix composites. All samples were about 5mm thick with approximately 0.84mm of thickness for the applied gel coat in coated samples. Prior to the outdoor environmental exposure, trimmed specimens were finally sealed on their edges using acrylic latex-based resin to restrain immediate moisture ingestion and hence more accurately simulate the large and flat composite sheets under outdoor exposure [37].

3.2 Experimental Procedure

After fabrication and curing of samples, select properties, such as surface roughness and hardness, flexural bending strength, and density, were immediately measured before the outdoor exposure. These properties were also frequently monitored during the natural ageing period, with measurements respectively performed at 30, 90, 180, 270, and 360 days after the installation of samples in the weathering station in Kelowna, BC, Canada. All mechanical tests were performed in a controlled laboratory environmental condition (at 21℃ and 33% of relative humidity (RH)). The ageing condition, as well as the equipment involved in the mechanical tests, are thoroughly delineated in the subsequent sub-sections.

3.2.1 Climatic Outdoor Exposure/ Weathering Station

As shown in Figure 3-1, trimmed samples were installed on an adjustable aluminium rack, located on an unobstructed building roof in UBC Kelowna Campus, and exposed to all possible
natural climatic agents. The orientation of the exposure rack was engineered to maximise the absorption of sunlight during the ageing period. Samples were installed with a flat mould side facing upwards, and with an inclination of 45° to prevent any potential pooling of water. Test specimen were also fixed manually on their edges, using some ultra-high molecular weight polyethylene clamps (Figure 3-2) to avoid contamination from the rack structure.

![Figure 3-1) The set-up used for the natural ageing of test specimens](image1)

![Figure 3-2) The fixture clamps made of ultra-high molecular weight polyethylene](image2)

Weathering station was installed adjacent to the exposure rack as depicted in Figure 3-1. The Campbell Scientific® weathering station was equipped with CR800 data logger, as well as several sensors, including relative humidity (RH) and temperature probes, broadband UV radiometer, and TE525 tipping bucket rain gauge.
3.2.2 Property Measurements/ Mechanical Tests

Using a Portable Surface Roughness Tester Qualitest™ TR110 (Figure 3-3), the mean value of surface roughness ($R_a$) was measured for each sample. The average value of roughness was determined from 10 randomly selected points on the exposed surface, in the midsection of each specimen. Measurements were performed on the flat mould side and in accordance with TR110 operating procedures.

![Figure 3-3] The portable surface roughness tester Qualitest™ TR110

In addition to the surface roughness, the Shore-D hardness was measured for each specimen, using a Stationary Qualitest™ HPE-II Durometer (Figure 3-4), and conforming to ASTM D2240-05 standard. The average value was found from measurements for three randomly selected points on the flat mould side and along samples midsection.

![Figure 3-4] The Stationary Qualitest™ HPE-II Durometer
Three-point bending (3PB) tests were only carried out on the reinforced test specimens to measure their flexural strength. These tests were performed under ASTM D7264/D7264M-07 standard, using the Instron 5966 Dual Column Testing Machine (Figure 3-5). Two tests were done at each monitoring stage, with the crosshead speed of $10 \text{ mm min}^{-1}$ and preloading of 35N. Preloading was required to stabilise samples, owing to the uneven surface of the open mould side of laminates. Flexural strength was calculated using Eq. (3-1), where $F$ is the applied load, $L$ the support span (changing based on samples thickness), $b$ the samples width, $h$ the sample thickness, and $\sigma$ the calculated flexural strength.

$$\sigma = \frac{3FL}{2bh^2} \quad (3-1)$$

![Figure 3-5) Instron 5966 Dual column testing machine](image)

One of the destroyed pieces of samples, destructed under the 3-point bending test, (roughly 50% of undamaged specimen total mass) was subsequently used to measure the density of aged GFRPs. These measurements were obtained using Qualitest™ MDS-300 densimeter, as shown in Figure 3-6.
Finally, to validate the ageing induced damages, the internal structure of aged samples was tomographically inspected using an Xradia micro-CT 400 scanner, as shown in Figure 3-7.

3.3 Principal Component Analysis (PCA)

As an exploratory multivariate data analysis method, Principal Component Analysis (PCA) was applied to the collected data to extract correlations between the degrading climatic agents and their resultant changes in the physical properties. Its implementation was also helpful to visualise how processing factors may affect the ageing behaviour of GFRP products. The explorative capabilities
of PCA systematically quantifies and visualises relations between the measured variables, besides the influence that a particular variable may have on each observation. In other terms, PCA not only provides an overview of correlations between variables but also its visualisation capabilities help us to gain a better insight into the causes and effects of degradation, under several climatic ageing factors.

Unlike many other multivariate data analysis techniques, like MANOVA, PCA is not limited to normally distributed datasets [94]. It is based on the dimensional reduction and projection of data to a reduced space. Principal Components (PCs) of this new space are generally identified form the covariance matrix of data and are defined as a linear combination of original variables, at directions along which the variation of data is maximised.

Observation matrix, $X_{n \times p}$, with $n$ observations and $p$ variables, normally form a swarm of data in the original space, with $x$, $y$, and $z$ as components in Figure 3-8. This matrix is commonly centred by moving the origin to the mean value of the dataset (centralisation); then, the impact of variance is standardised for each variable (normalisation). Normalisation is commonly carried out by dividing variables by their standard deviation ($s_i = \frac{1}{n-1} x_i^T x_i, \ i = 1, \ldots, p$) or, in other words, by scaling each variable ($X_{SC_{n \times p}}$, the centralised and normalised observation matrix).

Figure 3-8) An example showing the swarm of a dataset in a 3-dimensional space [95]
In the next step, eigenvalues of the Sample Covariance Matrix, defined in Eq. (3-2), are found, together with their corresponding eigenvectors. Eigenvalues of the sample covariance matrix represent the variation of data along the direction of their corresponding eigenvectors. A higher level of an eigenvalue implies a more significant variation of data along its equivalent eigenvector direction. Therefore, to minimise the resultant error from the dimensional reduction, the new space is defined by eigenvectors as its principal components, basically in the descending order of their corresponding eigenvalues. As an illustration, the first principal component (PC1) corresponds to the largest eigenvalue, the second principal component (PC2) corresponds to the second largest eigenvalue and so on.

\[ S = \frac{1}{n-1} X_{sc}^T X_{sc} \]  

(3-2)

The matrix consisting of the projected observations \((T_{n \times p})\), known as Score Matrix, is found using Eq. (3-3). \(P_{p \times p}\) in Eq.(3-3) defines the new space and is composed of the principal components as column vectors. This matrix is commonly called Loading Matrix, as its entities express the influence of each variable on principal components.

\[ T_{n \times p} = X_{sc_{n \times p}} P_{p \times p}, \]  

(3-3)

\[ P = [PC1, PC2, ..., PCp] \]

A large number of observations normally implies invertibility of sample covariance matrix (no null spaces in \(S_{p \times p}\)). Therefore, loading matrix, consisting of the covariance matrix eigenvectors, is broadly of the same dimension as the original space. Additionally, since the sample covariance
matrix is symmetric, the loading matrix is orthogonal, and no correlations do exist between the calculated principal components.\(^1\) Hence, scaled observations can be back calculated as follow:

\[
X_{SC_{n\times p}} = T_{n\times p} P^T \tag{3-4}
\]

To limit the risk of a complex model, a limited number of principal components are usually selected, yet with the cost of lost information in the model and its resultant error. This error is described by Noise Matrix \((E_{n\times p})\) in Eq.(3-5) \((q\) is the number of selected PCs).

\[
T_{n\times q} = X_{SC_{n\times p}} P_{p\times q} \tag{3-5}
\]

\[
X_{SC_{n\times p}} = T_{n\times q} P_{p\times q}^T + E_{n\times p}
\]

Frequently, just the first two principal components are selected for the analysis to facilitate the visual interpretation. It is often desirable to show scores and loadings (projection of original variables) on a plane consisted of these two PCs (Figure 3-9). In loading plots, variables are often represented as vectors, whose lengths indicate the impact of the corresponding variables on the PCs and accordingly on the variation of the whole data.

\[\text{Figure 3-9} \text{ An example showing the plane consisting of the first 2 PCs and inserted to the swarm of data}\]

\(^1\) Eigenvectors of a symmetric matrix constitutes an orthogonal matrix.
The angular closeness of variables (cosine of their angle) is denoting their correlation (Figure 3-10). Variables in the same direction are positively correlated, yet negative correlation exists between those reversely aligned (Figure 3-10-a and Figure 3-10-b). Also, perpendicular vectors in loading plots imply independence of the corresponding variables (Figure 3-10-c).

Comparison of loading and score plots is also helpful to extract further information. Observations located close to a vector in a score-loading plot are known to be more significantly affected by that variable. As an illustration, in Figure 3-9, regions separated by blue and red border lines are more influenced by variables named as $x$ and $y$ respectively.

Figure 3-10 Correlation between two variables, defined based on the cosine of their angles (a) direct correlation (b) negative correlation (c) independence of the variables
Chapter 4: Results and Discussion

4.1 Mechanical Performance over Ageing Span

As discussed in Section 3.2.2, select material properties were seasonally monitored for all types of samples, to investigate their weathering performance. The involved climatic degrading agents, whose average values are reported in Figure 4-1, were monitored during the whole ageing period started in February 2014 and lasted for one year (The data analysis section, which was the main purpose of this thesis started in January 2017).

(a) Temperature  
(b) UV index scale
In Figure 4-2, changes in surface roughness can be detected for all types of test specimens, either gel coated (GC) or uncoated (NG). Measurements corresponding to samples with chopped mat (C) and woven fabric (W) reinforcements are respectively marked by red and blue points, along with the measurements for the pure resin (R) samples which are depicted in grey points.

As shown in Figure 4-2-a, the application of surface coating dramatically limited the weathering induced shifts in surface roughness during our experiment. Thus, aligned with [83], surface quality can be effectively preserved by applying a thin protective layer of gel coat. After 180 days of natural ageing, both types of uncoated fibre reinforced samples were higher in their surface roughness compared to their unreinforced neat resin counterparts (Figure 4-2-b). The inferior
surface quality of uncoated reinforced samples may be justified by surface degradation, material leaching, and the eventual fibre blooming. This ageing induced rise in surface roughness is found to be even more dramatic for uncoated GFRPs with chopped mat reinforcements (Figure 4-2-b). Primarily, the lower fibre content in this type leaves the matrix highly prone to photodegradation [5, 82, 91]; then, seasonal precipitation and its resultant flow of water can lead to leaching of the degraded resin chains and exposure of fibres. Surface degradation and the resultant fibre blooming is clearly shown in Figure 4-3 for an uncoated chopped reinforced sample and after 270 days of its natural weathering.

![Figure 4-2) Changes in surface roughness for (a)Coated and (b) Un-coated samples during the ageing period; the dashed lines represent the trends for the average value, while the points depict each measurement](image)

In fibre reinforced composites, higher fibre content may contribute to the preservation of the material performance [82], as fibres hold the resin bulk [5] and hamper leaching of the polymeric chains. Fibres also retard the penetration of UV rays to the internal layers [91] and accordingly hinder photo-degradation. As a result, the higher fibre content in composites means an improvement in the retention of their properties during natural exposure. Apart from photo-oxidation caused by UV radiation in the proximity of oxygen [25, 84], hydrolysis reaction in moist
and humid conditions triggers scission of polymeric chains [53, 60]. Broken chains with lower molecular weight, and accordingly weaker intermolecular Van der Waals bonds are more susceptible to be leached from the resin chunk [17]. Thus, the interfaces imported by fibres and consequently, the higher potential for moisture ingression may justify the inferior surface quality of aged reinforced samples in Figure 4-2-b compared to their unreinforced counterparts.

![Figure 4-3](image.png)

**Figure 4-3** Weathering induced defects in a chopped reinforced sample, after 270 days of natural ageing

The advantage of gel coat in promoting surface quality is also detectable through hardness trends, as gel coat application similarly limited shifts in surface hardness during the exposure period (Figure 4-4-a). For all uncoated samples, hardness was mostly decreasing during the humid winter, with a relatively steeper drop experienced by woven types (between the days 180 and 270 in Figure 4-4-b).

The phenomenon known as plasticisation or resin softening (per Section 2.1.1.1) chiefly leads to the decline in hardness. Penetration of water molecules between polymeric resin chains enhances chains mobility, resulting in a softer matrix structure [53, 54]. Typically, matrix
plasticisation [9] is known as the dominant degradation processes among those that matrix may undergo [2, 62] and its effects are known to be recoverable after desorption [2, 37]. Signs of such recoverability can also be noticed in Figure 4-4-a and b under our natural weathering experiment.

![Graph showing changes in surface hardness for coated and un-coated samples during the ageing period](image)

**Figure 4-4** Changes in surface hardness for (a) Coated and (b) Un-coated samples during the ageing period; the dashed lines represent the trends for the average value, while the points depict each measurement.

In composites with continuous fibres, moisture sorption is through the combined action of diffusion in matrix and capillarity along fibres (along cracks at fibre-matrix interface regions) [2, 26]. These types of composites are proven to be more diffusive along their fibres rather than through their matrix structure [17, 56]. In these types, hydrolysis reaction contributes to the weakening of fibre-matrix bonds [54, 60]. Then, differential swelling stresses [23, 27, 58], together with the dissolution of fibres sizing in absorbed water [9, 61], ultimately leads to the interfacial debonding, the known prevalent damage among aged composites with woven fabric reinforcements [2, 26]. The additional free volume in woven types [2, 42, 51, 54, 55], imposed by interfacial debonding [41], means their more potential for moisture ingression, and thus, the sharper reduction of hardness during the wet and humid seasons (Figure 4-4-b).
All types of samples were generally gaining hardness during the sunny season of the ageing period (between days 30 and 180 in Figure 4-4-b). This hardness gain would be representative of post-curing and polymerisation of un-reacted monomers under the action of sunlight UV radiation [16, 17, 89, 90]. Indeed, before the outset of photo-degradation, the two latterly discussed phenomena (polymerisation and post-cure crosslinking) lead to the chains with higher molecular weight and stronger intermolecular bonds, ultimately resulting in a stiffer matrix structure.

Changes induced by UV radiation are also known to be dominantly limited to the irradiated surface [82] and more likely affect the measured hardness values. Naturally, the irradiated surface protects its underlying internal layers from UV radiation and invasion of oxygen [25]. As a result, applying a layer of coating, as a frontline barrier against UV, can effectively limit the ageing induced shifts in hardness (Figure 4-4-a). However, given the softer structure of the applied gel coat compared to the matrix, coated samples were generally of lower value in their hardness than their uncoated counterparts during this experiment.

![Changes in flexural strength for (a) Coated and (b) Un-coated samples during the ageing period; the dashed lines represent the trends for the average value, while the points depict each measurement.](image)
Similar to the trends of hardness, the rise in the flexural strength (Figure 4-5) was under the action of sunlight UV radiation (post-curing and polymerisation effect) in our experiment, while its drop (Figure 4-5) was vastly under the influence of moisture ingestion (plasticisation and affected interfacial bonds). For coated samples, the decline in the flexural strength, experienced within the first 30 days of ageing (Figure 4-5-a), was probably due to debonding of the coating from the resin bulk. Indeed, the additional interface imposed by veils and coatings, together with their subsequent debonding, may inflict moisture uptake in coated composites, leading to the degradation of constituents [40]. This decline was found to be even sharper for coated samples with continuous fibres, where the debonding also followed the fibre path.

Unlike the decreasing trends of hardness, all uncoated fibre reinforced samples, with either chopped or continuous fibres, were declining in their flexural strength, with quite similar slopes, during the humid season (see Figure 4-5-b in the interval between the days 180 and 270; also, compare it with Figure 4-4-b in the same interval). Two distinct mechanisms are found here to degrade the flexural properties in these two types, but with quite similar impacts (Also see 4.3). The weakened fibre-matrix bonds, due to moisture absorption, lead to the decline in flexural strength for composites with continuous fibres [2, 26], while for chopped fibre reinforced GFRPs, matrix degradation (ageing induced bubbles and microcracks in the matrix as shown in Figure 4-3) is known as the chief cause of this reduction [96].

Photo-degradation leaves the material with lower density on its outer layers, as UV mostly affects the irradiated surface. The resultant density gradient in the composite induces differential density stress in the material structure [13, 36], leading to the formation of microcracks. Diurnal temperature variation is another climatic factor known for the initiation of microcracks [84]. As fibres and matrix differ in their thermal expansion rates, daily variation in temperature results in
internal thermal stress and ultimately in the generation of cracks. UV radiation may also increase the void content in the composite structure. Visible bubbles may form and expand in the material structure as a by-product from chemical reactions and photo-degradation [82]. This additional void content intensifies the degradation of flexural properties.

The lower fibre content in chopped samples suggests a higher rate of matrix degradation, a higher density of microcracks, and more frequency of bubbles in the material, compared to their woven counterparts. Fibres, firstly, contribute to holding the resin chunk [5] and hindering the initiation of cracks. Fibres also retard UV radiation and make the composite more resistant against photo-degradation.

4.2 PCA Analysis of Measured Properties and Environmental Data

PCA analysis, as a multivariate exploratory data analysis technique, is applied to the measured properties and environmental data over the exposure time. Both observations and variables were projected onto a plane, consisting of the first two principal components (PC1 and PC2). Observations are displayed as points (scores) in their respective colour (based on their category), together with variables, presented by vectors (loadings) in score-loading plot figures.

4.2.1 Effect of Design and Process Variables on Properties

Firstly, the select design and processing (controlled) variables were investigated, and their effect on the weathering performance of GFRP composites were found. The investigated design and processing variables were as follows: 1) the reinforcement architecture (either chopped mat or woven fabric) 2) the coating application (either coated or uncoated) 3) the initial curing state (either cured in an oven or cured ambiently). Apart from these variables, climatic factors (uncontrollable variables) were also analysed and correlated with the select material properties, such as surface
roughness and hardness, flexural strength, and part density (specific gravity (SG)). These correlations, describing the weathering performance of the material, helped us to find the main underlying causalities for degradation effectively.

As PCA is only capable of dealing with numeric variables, discrete variables were used to describe design and processing (controlled) variables, i.e., each of these variables was coded by a digit. As an illustration, the chopped mat (C) and the woven fabric (W) reinforcements were coded as “1” and “2” respectively, similar to the curing process in the ambient lab condition (PC, “1”) and curing process in an industrial oven (FC, “2”). The application of surface coating was also coded similarly if the gel coat was or was not applied (uncoated (NG) and coated (GC) samples were respectively coded as “1” and “2”).

![Figure 4-6) Effects of different design and processing variables on the natural weathering of GFRPs; notice the clear clustering of different composite types; points denote measurements during the exposure period.](image)

The analysis reveals that by shifting from the chopped mat to woven fabric as reinforcement, flexural strength is increased in the product (see the positive correlation between “Reinforcement”
and “Flexural” axes in Figure 4-6). The higher fibre content in woven types implies their higher density and superiority in their flexural properties.

As discussed earlier in 4.1, the surface degradation induced by weathering can be effectively limited by applying a thin protective layer of gel coat. This effect can be detected in Figure 4-6, by the negative correlation of “Coating” axis with both “Roughness” and “Hardness” variables. These correlations are aligned with the results in 4.1, as uncoated samples are found to be broadly rougher and harder (more brittle) than their coated counterparts. Applied gel coat can normally block the UV rays and hinder their penetration to the main bulk of the material; thus, hindering post-curing and retarding the surface degradation in the material structure.

Compared to the two formerly discussed design factors, the initial curing state is found to have minor effects on the weathering performance of GFRP composites. As discussed earlier in Chapter 3, the Degree of Cure (DOC) was estimated to be in close ranges for both investigated curing states (96% and 84% respectively for samples cured in an oven and those cured ambiently), resulting in similar weathering trends for both cases.

4.2.2 Effect of Climatic Agents on Measured Properties

Apart from design and processing variables, climatic agents are also analysed in this section, and their effect on the weathering performance of GFRP products are investigated. Effect of exposure time is also studied to see how the interaction of these agents may affect GFRP composites at the prolonged outdoor exposures. Climatic agents included in the analysis, per Figure 4-1, are as follows: 1) UV Radiation (UV Index Scale), 2) Environmental Temperature (°C), 3) Average Precipitation Level (mm) 4) Average Snow Level on the Ground (cm), 5) Relative Humidity (RH%). These variables are represented by vectors in score-loading plot figures (Figure
4-7 to Figure 4-14), respectively named as “UV”, “Temp”, “Precipitation”, “Snow”, and “RH”. In addition, vectors named as “Time” and “SG” refer to Ageing Time (days) and Sample Density \( (gr/cm^3) \) (Specific Gravity), respectively.

Among the soaking agents (“Snow” and “RH”), the depth of snow cover on the ground signifies moisture ingestion in liquid form, yet relative humidity may represent penetration of water molecules in gaseous status. As snow gradually thaws out, composites have enough time to absorb water when covered by a layer of snow. Seasonal precipitations, on the other hand, are expected to affect visual properties in a broader context, with negligible effects on moisture sorption. Primarily, evaporation of water, after these precipitations, hinders the considerable amount of water uptake. Therefore, compared to the precipitation level, immersion under snow is deemed to be a more affecting agent in moisture sorption.

![Figure 4-7) Effect of climatic agents on the performance of aged samples](image)

**Figure 4-7) Effect of climatic agents on the performance of aged samples**

Congestion of observations around the “UV”, “Temp”, “RH”, and “Snow” axes in Figure 4-7 indicates the more significant effect of these variables on the weathering of GFRPs, rather than the precipitation level. Observations accumulated around “Precipitation” axis are mainly related to
uncoated chopped reinforced categories, signifying higher impact of seasonal precipitations on these types. Uncoated chopped reinforced samples are also found to deviate from their other counterparts at some ageing stages. This deviation, chiefly on the roughness axis, is denoting the effect of gel coat application for this type to achieve a better surface quality.

The direct correlation of roughness with both ageing time and precipitation level in Figure 4-7 means inferior surface quality after prolonged natural ageing and under seasonal precipitation. Indeed, exposure to UV radiation leads to photo-degradation and accordingly high density of broken chains on samples surfaces. Then, seasonal precipitations and their resultant flow take part in degraded chains leaching, and accordingly fibres exposure.

Effects of both post-curing and polymerisation are also implicitly discernible in Figure 4-7. Particularly, close and positive correlation of mechanical properties (hardness and flexural strength) with both UV radiation and environmental temperature denotes stiffening and hardening of samples when aged by these agents. Among these two agents and aligned with [17], UV is found to have a higher correlation with rises in mechanical properties, revealing more effect of UV radiation on post-curing rather than temperature increase.

As a clue to moisture ingression side-effects, such as matrix plasticisation and weakened interfacial bonds (discussed in Section 4.1), “RH” and “Snow” are reversely correlated with mechanical properties (Figure 4-7). Snow immersion mainly degrades the flexural strength, while “RH” is notably involved in the loss of surface hardness. The greater impact of snow immersion on flexural strength is presumably indicating the increased risk of decayed interfacial bonds when absorbed water is liquid. On the other hand, penetration of water molecules in gaseous status mostly facilitates mobility of polymeric chains and therefore broadly leads to the matrix plasticisation.
Overall, both UV radiation and moisture ingression have mitigating effects on each other [5]. Namely, UV radiation energy is dissipated through the removal of absorbed moisture or its evaporation, making saturated composites less prone to photo-degradation. Further, in the exposure of UV radiation and before the outset of photo-degradation, the irradiated surface starts to shrink (crosslinking or post-curing effect). As the inner layers of a composite laminate are protected from UV rays, this shrinkage is hindered by unexposed layers. The resultant internal (residual) compressive stress promotes fibre-matrix bonding and also alleviates swelling of the matrix. Therefore, UV radiation makes up for repercussions of moisture ingression.

4.2.2.1 Weathering Patterns for GFRP Composites with Different Fibre Architectures

To obtain a better insight into the weathering performance of GFRP composites, samples are analysed in the coming subsequent sections based on the design and processing variables. Comparison of samples based on their reinforcement architectures firstly reveals the better surface quality of aged woven types. Indeed, the passage of time was less dramatically sensed in their appearance during our experiment (compare the positive correlation between “Roughness” and “Time” axes in Figure 4-8-a and b). Also, the effect of seasonal precipitation on surface roughness was less damaging for this category than their chopped counterparts (compare the positive correlation between “Roughness” and “Precipitation” in Figure 4-8-a & b). The superior surface quality of woven reinforced composites is presumably the consequence of their higher fibre content, holding the resin chunk and deferring its degradation.

As an evidence to water uptake, exposure to humid and snowy climatic conditions led to rising in density for all categories, with either continuous or chopped reinforcements (see the correlation of “SG” with both “RH” and “Snow” variables in Figure 4-8-a & b). In the case of composites with continuous fibres, this water uptake chiefly resulted in decayed bonds at fibre-matrix
interfaces, specifically when the absorbed water was in its liquid phase. These weakened interfacial bonds are evidenced for the aged woven category in Figure 4-8-b, by the negative correlation between flexural strength and snow level. Here, the strong inverse correlation between these two variables denotes the significant risk of interfacial debonding for composites with continuous fibres.

![Weathering patterns in reinforced categories](image1)

**a) Chopped**

![Weathering patterns in woven category](image2)

**b) Woven**

![Weathering patterns in neat resin](image3)

**c) Neat Resin**

Figure 4-8) Weathering patterns in both reinforced (either chopped or woven) and unreinforced samples

Contrarily, for chopped fibre reinforced samples (Figure 4-8-a), shifts in flexural strength are relatively independent of snow level. Independence of these two variables signifies that moisture ingression pattern was dominantly through resin in this category, without a significant effect on interfacial bonds. Indeed, narrower fibre-matrix interface region in chopped reinforced composites
makes them less susceptible to fibre-matrix debonding, compared to the GFRPs reinforced with continuous fibres.

Comparison of chopped GFRPs with unreinforced (neat resin) samples also leads to similar results. In Figure 4-8-a (chopped category), the correlation of “Hardness” with both “RH” and “Snow” variables is analogous to those in Figure 4-8-c (unreinforced samples). Particularly, the surface hardness is nearly independent of snow level and is inversely correlated with relative humidity in both cases (showing the effect of matrix plasticisation in humid environments). This resemblance among correlations reinforces the hypothesis that moisture ingestion is chiefly through resin for chopped reinforced GFRPs and not affecting fibre-matrix interfacial bonds.

Overall, design with continuous reinforcements seems to be a better decision for long-term outdoor applications. The higher potential for moisture uptake in woven types does not mean their inferior quality from the mechanical point of view, as on average, they have demonstrated better performance during their ageing (see the trends in Figure 4-4 and Figure 4-5). Also, more potential for moisture sorption in these types, along with their higher fibre content, means their more resistance against photo-degradation.

4.2.2.2 Effects of Coating Application on GFRP Weathering

In this sub-section, weathering patterns are analysed and compared based on the application of surface coating. The results shown in Figure 4-9 reveal the effect of this design variable on limiting the absorption of moisture in the liquid phase. In this experiment, mechanical properties for coated samples, namely flexural strength and surface hardness, were less significantly affected by immersion under a snow cover, compared to uncoated counterparts (see the correlation of “Snow” with “Flexural” and “Hardness” axes in Figure 4-9-a and compare it with that in Figure 4-9-b).
Hence, apart from boosting surface quality (as shown in Figure 4-2), application of the isophthalic polyester resin, as a surface coating, can also inhibit water uptake.

This gel coat treatment, however, may fail to restrict the impact of humid environments on GFRP plates. As shown in Figure 4-9-a, relative humidity (RH) was still risking surface hardness of aged samples, even when the coating was applied (Notice the correlation between “RH” and “Hardness” in Figure 4-9-a and b). Indeed, water molecules are more mobile when they are in gaseous status [3, 64] and can penetrate in the molecular structure of the gel coat. By their entrance between polymeric chains, chains become more mobile, and coating structure becomes softer [2, 37, 53, 54].

![Figure 4-9) Comparison of weathering patterns between coated and un-coated samples](image)

The density of composites is known to be more dominantly affected by changes in the fibre content, rather than the moisture sorption effect. As a result, the correlation of density with all climatic agents may be implied to be irrational in Figure 4-9-a and b, where observations were not separated based on their reinforcement architecture. Therefore, filtering observations based on their reinforcement architecture, as shown in Figure 4-10 and Figure 4-11, would be beneficial to gain a better insight.
For composites with chopped mat reinforcements, the application of the surface coating can be an effective solution to limit both surface degradation and moisture uptake. The passage of time was less significantly sensed in roughness values for this type when gel coat was applied (see the correlation of “Time” with “Roughness” axis in Figure 4-10-a and compare it with that in Figure 4-10-b). The effect of seasonal precipitation on surface quality was also limited; therefore, gel coat treatment can be a practical solution for this architecture of fibres to achieve a better surface quality.

![Figure 4-10) Comparison of weathering patterns between coated and un-coated chopped samples](image)

The gel coat film can also limit the degradation of mechanical properties for chopped fibre reinforced GFRPs, either when exposed to humid environments or when immersed under a snow cover. As discussed earlier, moisture ingestion is dominantly through the matrix media for this architecture of fibres, without significant effects on the fibre-matrix interfacial bonds. Thus, this gel coat film can effectively limit the depth of moisture penetration, and accordingly limit the moisture sorption side-effects on flexural strength (see the correlation of “Flexural” with “Snow” and “RH” in Figure 4-10-a and compare it with that in Figure 4-10-b). The applied gel coat, however, may fail to sizeably cancel out the effect of moisture sorption on surface hardness, as the material used for the coating may plasticise and soften (see the correlation of “Hardness” with both “RH” and “Snow” axes in Figure 4-10-a). In this experiment, as shown in Figure 4-10, flexural
strength was affected by relative humidity in aged chopped samples, either coated or uncoated (see the correlation of “Flexural” with “RH” in Figure 4-10-a and b), as gas molecules are mobile and accordingly can penetrate more deeply in the material structure.

For composites with woven fabrics as reinforcement, the gel coat treatment may fail to remarkably limit the repercussions of snow immersion on flexural strength (notice the correlation of “Flexural” and “Snow” in Figure 4-11-a). The ageing induced decay at fibre-matrix interfacial bonds is primarily a major concern in this category, which cannot be negated simply by the application of the surface coating. Debonding of the applied gel coat from the material bulk may also raise new concerns [40]. This peeling of gel coat can lead to the additional free volume which moisture may invade; then as discussed in Chapter 1:, the absorbed moisture may penetrate to the bulk of the material, leading to further degradation of interfacial bonds.

**Figure 4-11) Comparison of weathering patterns between coated and un-coated woven samples**

Although surface coating may fail to substantially restrict degradation at interfacial bonds in GFRP composites with continuous fibres, its application can effectively limit the moisture ingestion through the matrix. In this experiment, as shown in Figure 4-4-a, hardness values were experiencing a levelling out for coated composites with woven fabric reinforcements. This small variation of hardness during the ageing period can be a clue to the limited effect of matrix plasticisation for these coated GFRP composites with continuous fibres. Presumably, this
application of gel coat on woven types may adequately offset the weathering induced variations in
density and surface hardness (noticeable from the small size of vectors for “Hardness” and “SG”
variables in Figure 4-11-a).

4.2.2.3 Effect of Curing Process on GFRP Weathering

The two curing conditions involved in this study, as explained earlier in Sections 3.1, are
estimated to be in close values for their DOC (84% and 96% respectively for ambiently and in-
oven cured samples). Therefore, among the select processing and design variables, the curing state
has proven in Figure 4-6 to have a minimal effect on the weathering performance of GFRP plates.
To gain a more fine-tuned cure-based analysis of samples, comparison of weathering patterns is
obtained in this section based on the involved initial curing state.

The results shown in Figure 4-12 suggest the higher potential of ambiently cured GFRP samples
to absorb moisture. As demonstrated by this figure, the effect of snow level on mechanical
properties was less damaging for the composite plates cured rapidly at elevated temperature (notice
the correlation of “Snow” with both “Flexural” and “Hardness” axes in Figure 4-12-a and compare
it with that in Figure 4-12-b). Also, at prolonged exposure and under the effect of seasonal
precipitation, these highly cured samples retained their surface quality more effectively (see the
correlation of “Roughness” with both “Time” and “Precipitation” axes in Figure 4-12-a, and
compare it with that in Figure 4-12-b). This category, however, was not sufficiently resistant to
humid environments, that is the invasion of gas water molecules (notice the negative correlation
of “RH” with both “Flexural” and “Hardness” variables in Figure 4-12-a).

Curing rapidly at elevated temperature, therefore, may lead to a better retention of surface
quality for outdoor applications, along with the higher resistance against moisture invasion (uptake
of water molecules in their liquid phase). The higher level of DOC for GFRP composites cured at the elevated temperature potentially means the stronger bonds between their polymeric chains, yielding higher resistance to material leaching and better retention of surface quality. With higher DOC, lower level of moisture sorption is also expected for GFRP composites, as the more intense cure of the matrix makes its molecular structure more compact. This curing state, yet, may fail to significantly promote resistance to humid environments, as the gaseous phase of water molecules implies their greater mobility and accordingly their easier penetration [3].

![Comparison of weathering patterns between ambiently cured and in-oven cured samples](image)

**Figure 4-12) Comparison of weathering patterns between ambiently cured and in-oven cured samples**

The higher level of DOC, however, is not always desirable, specially when the long-term natural weathering is a major concern. Hence, for intensive outdoor applications, cure in the ambient temperature and pressure may be a sensible processing decision to reasonably postpone the start of photodegradation. Composites cured in this state, firstly, need more energy to reach their ultimate degree of cure, the point after which the degradation may start [97]. Secondly, the higher rate of moisture ingestion for ambiently cured composites mitigates the photodegradation side effects. As discussed earlier in this section, the energy of UV rays can be dissipated through the evaporation of absorbed moisture and thus, the resultant photodegradation may be eventually delayed.
In addition to deferring photodegradation, cure in ambient temperature can also lower the risk of interfacial debonding during the long period of natural ageing. For composites cured in ambient condition, more ductility is expected rather than those cured at the elevated temperature, and consequently, higher resistance to fibre-matrix debonding can be anticipated. Indeed, the matrix structure becomes more brittle in GFRP composites as their DOC is increasing. This brittle structure of the matrix implies the higher potential for generation of internal cracks and their eventual propagation along fibres [2, 97]. As a result, the risk of interfacial debonding soars when composites are cured rapidly in an industrial oven.

Overall, deciding on the curing process is one of the critical tasks in high tech composite industries, as it is dependant upon various processing and design variables. To obtain a better insight into the influence of curing condition over the weathering performance of composite products, it was deemed practical in this research to apply a cure-based analysis on the tested GFRP samples, against their reinforcement architecture (Figure 4-13 and Figure 4-14).

![Figure 4-13](image_url)

**Figure 4-13)** Comparison of weathering patterns between chopped reinforced samples with different curing states: a) cured in the industrial oven b) cured in the ambient condition

For GFRP composites with chopped fibres, curing at elevated temperature may significantly limit the adverse effects of moisture uptake on mechanical properties (compare the Figure 4-13-a
with Figure 4-13-b, regarding the correlation of mechanical properties, like “Flexural” and “Hardness”, with both “RH” and “Snow” axes). Indeed, moisture uptake would be dominantly through the matrix for this architecture of fibres, and the deeper penetration of moisture means the sharper degradation of mechanical properties. Limiting the depth which moisture may invade, cure in an industrial oven can offset the mechanical decline.

![Figure 4-14) Comparison of weathering patterns between woven reinforced samples with different curing states: a) cured in the industrial oven b) cured in the ambient condition](image)

For woven types, on the other hand, moisture sorption can comparably affect the mechanical properties, either when cured at the elevated temperature or in the ambient condition (see the correlation of mechanical properties, namely “Flexural” and “Hardness”, with “Snow” and “RH” in Figure 4-14-a and b). A broader fibre-matrix interfacial region in these GFRP types, and accordingly their higher potential for fibre-matrix debonding, imposes the risk of decline in their mechanical properties under moisture invasion. This effect seems to be enhanced further for those cured in the industrial oven, presumably owing to the higher level of DOC and the more brittle structure of the matrix, when cured at the elevated temperature (see the correlation between “Flexural” and “Snow” axes in Figure 4-14-a and b).

To decide upon the optimal curing state, as one of the most challenging engineering tasks in composites manufacturing, the weathering induced variations in material properties should be
taken into account (Figure 4-15 and Figure 4-16). A curing condition, leading to a greater level of stability in the long-term weathering performance of each given category (i.e. less variation of measured properties over the ageing period), would be considered as its optimal curing state.

Figure 4-15) Variations in properties during the ageing period, for chopped reinforced samples with different curing states

Figure 4-16) Variations in properties during the ageing period, for woven reinforced samples, with different curing processes

Considering such stability, curing in ambient condition seems to be a better option for GFRP composites with either reinforcement architecture (chopped mat or woven fabric), rather than curing in the industrial oven (see Figure 4-15 and Figure 4-16). As discussed earlier in this section,
gradual curing may lead to a more ductile structure of the matrix, lowering the risk of interfacial
debonding. Also, more potential for moisture ingress in ambiently cured samples means the
dissipation of UV radiation energy, and accordingly the reduced risk of photodegradation. Effect
of ambient curing state on limiting the matrix related degradations can be more significantly sensed
in chopped reinforced samples, whose weathering is dominantly through their matrix structure
(See Figure 4-15, the weathering induced changes in mechanical properties, namely hardness and
flexural strength, were less significant among the “C_PC” category than the “C_FC” type in Figure
4-15-a and b).

For coated composites with chopped mat reinforcements, although curing at elevated
temperature may effectively preserve the surface quality (see the variations in “Roughness” axis
in Figure 4-15-a), weathering induced changes in mechanical properties can be limited more
significantly when the ambient curing condition is selected at the fabrication stage. (notice the
more significant variations in “Flexural” and “Hardness” axes, in Figure 4-15 for the “C_FC”
category than the “C_PC” type). Thus, manufacturers may rationally compromise over the surface
quality to retain the mechanical properties for long-term outdoor applications. The inferior surface
quality of these ambiently cured samples can be attributed to their higher potential for moisture
uptake, imposing the risk of matrix swelling and affecting their surface quality.

For GFRPs with woven fabric reinforcements, however, matrix swelling should not be as
desperate since the high fibre content holds the matrix structure and prevents its swelling.
Compared to swelling of the matrix, surface quality is therefore broadly affected by the matrix
photodegradation in this type, whose effect can be mitigated by ambient curing at the fabrication
stage. This can be detected in Figure 4-16-a and b, where the weathering induced variations in
surface roughness were less significant among samples cured ambiently, regardless of their coating application.

The ambient curing state can also limit the weathering induced interfacial debonding in GFRPs with continuous fibres. In our experiment, as shown in Figure 4-16-b for uncoated samples with woven fabric reinforcements, ageing induced variations in mechanical properties, namely surface hardness and flexural strength, were less significant among those samples cured ambiently.

4.3 Visual and Microtomographic Inspection

To validate the involved degradation mechanisms discussed in Sections 4.1 and 4.2, GFRP plates were inspected in this section both visually and morphologically. Only samples cured at the elevated temperature were selected for these inspections to avoid the clutter of images. Unlike the visual inspections, which were carried out for both unaged and aged GFRP plates, the Micro-CT tomographic observations were only restricted to one-year aged samples. Using the Xradia micro-CT 400 scanner (shown in Figure 3-7), several forms of internal degradation were evidenced for different types of GFRP plates after one year of their natural ageing.

![Figure 4-17](image.png)

Figure 4-17) Alteration in colour and glossiness for unreinforced neat resin samples, after one year of natural ageing

The first significant change evidenced for almost all types of samples was their alteration in both colour and glossiness after the natural ageing period. This transition of colour, observable in Figure 4-17, is presumably attributed to the matrix degradation and shifts in its chemical
composition. As shown in this Figure 4-17, unreinforced samples, composed of neat polyester resin, became darker and less glossy after one year of their outdoor exposure.

Figure 4-18) Mould side of (a) unaged and (b) aged uncoated chopped samples

Figure 4-19) Mould side of (a) unaged and (b) aged uncoated woven samples

Figure 4-18 and Figure 4-19 depict the flat mould side (exposed side) of samples respectively with chopped mats and woven fabrics as reinforcement. Fibres protruded from the exposed surface of aged GFRP plates (shown in Figure 4-18-b, Figure 4-19-b, and Figure 4-20) are signifying the matrix surface degradation for both types during the ageing period. This weathering induced exposure of fibres, however, was more intense for the chopped category of samples (shown in Figure 4-18-b) than the woven category (shown in Figure 4-19-b). Natural weathering also led to the expanded and more extensively distributed bubbles through the GFRP plates, specifically through the chopped category (Figure 4-21-b). Consequently, woven samples have shown a better resistance to matrix degradation than their chopped counterparts, as the additional fibre content in the former case contributes to holding the resin chunk and subsequently to retarding the matrix
degradation. The results obtained from these visual inspections are well consistent with the PCA results discussed in 4.2.2.1.

![CT-Tomography inspection from the exposed surface of an uncoated woven sample](image)

**Figure 4-20** CT-Tomography inspection from the exposed surface of an uncoated woven sample

![Bubbles and internal defects in (a) unaged and (b) aged uncoated samples with chopped fibres; bubbles expanded due to natural ageing are marked by red circles in (b)](image)

**Figure 4-21** Bubbles and internal defects in (a) unaged and (b) aged uncoated samples with chopped fibres; bubbles expanded due to natural ageing are marked by red circles in (b)

Although surface degradation is a major concern in composites with either type of fibre architecture, the application of gel coat can significantly improve the surface quality. As shown in Figure 4-22 and Figure 4-23, no remarkable differences did exist between the aged and unaged
status of coated GFRP plates with either architecture of fibres. This is properly aligned with the results discussed thoroughly in 4.1 and 4.2.2.2.

Figure 4-22) Mould side of (a) unaged and (b) aged coated samples with chopped fibres; no major changes were detectable on the exposed surfaces after natural ageing

Figure 4-23) Moulded side of a) unaged and b) aged coated samples with woven fabrics; no changes were detectable on the exposed surface after natural ageing

For an uncoated woven sample, shown in Figure 4-24-b, internal cracks were visually detectable along the fibre bundles after one year of outdoor exposure. These cracks, which were barely visible in the unaged woven type (shown in Figure 4-24-a), signify the weathering induced fibre-matrix debonding. Fibres separated from their surrounding resin are also seen in Figure 4-25-b at the cross-section of an aged woven sample. These visible cracks, however, were only ambiguous evidence for the fibre-matrix debonding and the precise observation of this phenomenon was not obtained. To empirically observe this interfacial debonding and to scan the internal defects more clearly, X-ray microtomographic scanning was accordingly adopted. After the tomographic inspection, as shown in Figure 4-26, several affected regions were more accurately uncovered for a one-year aged uncoated woven sample.
Figure 4-24) Internal structure of (a) unaged and (b) aged uncoated samples with woven fabrics as reinforcement; faded areas denote internal cracks either along their length (blue boxes) or across their width (red boxes).

Figure 4-25) Cross-section of (a) unaged and (b) aged uncoated samples with woven fabrics as reinforcement; cracks across the width (marked by red arrows) are denoting interfacial debonding after ageing.
Figure 4-26) Micro-CT inspection of an uncoated woven sample, after one year of natural ageing and before the destructive 3-point bending test; red arrows represent regions with interfacial debonding.

Figure 4-27) Micro-CT inspection of an uncoated woven sample, naturally aged for one year and destroyed after a 3-point bending test; red boxes represent regions with weak interfacial bonds (cracks propagating along fibre bundles), as opposed to the blue box where interfacial bonds have not been affected by ageing (cracks spreading through fibre bundles and not affecting the fibre-matrix interfaces)
For those aged woven samples destroyed by the 3-point bending test, several regions were detected again embracing cracks along fibre bundles (regions marked by red boxes in the tomographic image in Figure 4-27). This mode of failure indicates weak interfacial adhesion at the affected regions, as cracks were not propagating to the surrounding resin and were broadly developing along the fibre-matrix interfaces [98, 99]. These observations reinforce the hypothesis that the differential swelling stress leads to the decay at the fibre-matrix interfacial bonds and ultimately the propagation of cracks along these affected interfaces [2, 58].

For coated samples, peeling of the applied gel coat is another concern. As also discussed in 4.2.2.1, cracks may propagate along the additional interface between the thin layer of gel coat and the material bulk [40], leading to the ultimate peeling of the coating film. Destructive agents, such as water and oxygen molecules, may subsequently invade at the resultant free volume and contribute to the degradation of the GFRP plates. This peeling of the gel coat film has been verified in Figure 4-28 for a coated sample of the woven type, after 30 days of its natural ageing.

![Micro-CT image of a coated sample with woven reinforcement, after 30 days of natural ageing; red arrows represent fibre-matrix interfacial debonding (cracks along fibre bundles); blue arrows denote debonding of the coating film from the material bulk.](image)

Figure 4-28)
Consequently, unlike the surface degradation which was effectively limited by applying a coating layer (see the roughness trends in Figure 4-2), this gel coat treatment has failed to fully inhibit the ageing induced fibre-matrix debonding effect, specifically for GFRP plates with continuous fibres. Longitudinal cracks along the edge side of the aged woven samples, as shown in Figure 4-29, suggest the weathering induced interfacial debonding as a serious concern for the long-term performance of this type, even when the surface coating was applied. Tomographic inspection, shown in Figure 4-28, has also verified these ageing induced cracks developed along the continuous fibre bundles.

![Coated samples with woven fabrics as reinforcement shown at their edge side in their (a) unaged and (b) aged status; the longitudinal cracks in the aged sample (narrow white lines along its length) indicate the fibre-matrix debonding](image)

Figure 4-29) Coated samples with woven fabrics as reinforcement shown at their edge side in their (a) unaged and (b) aged status; the longitudinal cracks in the aged sample (narrow white lines along its length) indicate the fibre-matrix debonding

Fibre-matrix debonding, however, is not a serious weathering concern for the GFRP composites with the chopped mat as reinforcement. As shown in Figure 4-30 and Figure 4-31 for the chopped category, longitudinal cracks were barely visible at the edge sides, either in the aged or unaged status of samples and regardless of the surface coating application.
Figure 4-30) Uncoated samples with chopped mat as reinforcement shown at their edge side in their (a) unaged and (b) aged status; longitudinal cracks were barely visible regardless of ageing

Figure 4-31) Coated samples with chopped mat as reinforcement shown at their edge side in their (a) unaged and (b) aged status; longitudinal cracks were barely visible regardless of ageing

Formation of microcracks and expansion of bubbles are other trigger points for the long-term outdoor application of GFRP parts. Prior to their outdoor exposure, the selected manufacturing process is typically well-known to be responsible for the formation of bubbles in the matrix structure. During their service, however, climatic agents, and more specifically UV radiation, also take part in both the formation and the expansion of bubbles. Therefore, long-term outdoor exposure of these materials may lead to a rise in their void content and accordingly, a steeper decline in their mechanical properties [82].
Compared to GFRP plates with woven fabrics as reinforcement, the lower fibre content of those with chopped fibres inherently means their higher potential for matrix degradation. The weathering induced expansion of bubbles, clearly demonstrated in Figure 4-32, is therefore expected to be more severe for these chopped fibre reinforced GFRPs and is deemed to be the underlying cause of the decline in their flexural properties [96] (Also discussed in 4.1 for the weathering performance of uncoated chopped samples and the decline involved in their flexural properties).
This matrix degradation, however, seems to be limited when a thin layer of isophthalic resin is applied on the surface. As shown in Figure 4-33, bubbles detected in the aged coated samples were of smaller size compared to their uncoated counterparts and were also less frequently distributed after the long-term outdoor exposure. As a result, this surface treatment may effectively limit the weathering induced a decline in flexural properties (demonstrated in Figure 4-5-a and Figure 4-5-b) for randomly oriented GFRPs with discontinuous fibres, in addition to improving their surface quality for long-term outdoor applications. For woven fabric reinforced GFRPs, on the other hand, this surface treatment mainly promotes visual appearance without a significant impact on their micro-structural performance.
5.1 Conclusions

Long-term durability of FRP composites has often been a controversial subject in both academia and industry. In this research, a comprehensive experimental-statistical analysis was performed to study the weathering induced changes in different types of GFRP composites, along with the degradation processes involved in their natural ageing. The study was primarily carried out to address the considerable gap in the literature on how unprotected exposure to natural climatic conditions may affect both visual and structural performance of this material.

Polyester based test specimens, including reinforced and unreinforced samples, were provided in ten different types, eight of which were reinforced GFRPs. GFRP plates, varying in their fibre architecture, the application of the surface coating, and their initial curing condition, were all exposed to a natural semi-arid climate for one year in Kelowna, BC. Unreinforced samples, only varying in their curing state, were also aged in the same environment to explore the degradation processes involved in the matrix structure.

Several climatic agents were monitored during the ageing span, along with the select material properties, such as density, surface roughness, surface hardness, and flexural bending strength,
which were seasonally measured and compared. To extensively study the effect of long-term outdoor exposure, PCA was adopted as an exploratory data analysis technique, and the relative contribution of each climatic agent was effectively determined for each type. In the end, the select samples were inspected both visually and morphologically to validate several degradation processes involved in the natural ageing. The internal structure of aged samples was carefully inspected by the X-ray tomography scanning, and the affected regions were clearly detected for each type.

The most affecting climatic agents were found, and their outcomes are summarised as follows:

- Among the several climatic agents to which samples were exposed during natural ageing, sunlight UV radiation, relative humidity (RH%), and the depth of snow cover on the ground (cm) were found to be the most damaging climatic variables.
- UV radiation was usually responsible for surface photo-degradation although a short period of exposure to this agent could lead to post-curing and hardening of the matrix structure.
- Development of microcracks and expansion of bubbles were other outcomes of long-term UV irradiation. GFRP composites with lower fibre content were found to be highly sensitive to this climatic agent.
- Relative humidity and the depth of snow cover, both representing the uptake of water molecules, but respectively in their gas and liquid phase, could result in the consistent degradation of structural properties. Unlike UV radiation, whose effects were mostly concentrated on the irradiated surface with visually observable outcomes (e.g. alteration of colour and glossiness, as well as a rise in the level of surface roughness), water uptake
was affecting the internal structure of the material, with typically far-reaching impacts on mechanical properties.

- Moisture uptake when samples were immersed under a snow cover (uptake of liquid water molecules) mostly affected the fibre-matrix interfacial bonds, especially for samples with continuous fibres.

- Exposure to relatively humid conditions on the other hand, mostly degraded the surface hardness, as gas water molecules penetrated the matrix molecular structure, and made it softer (the effect of plasticisation by the penetration of gas water molecules). The effect of matrix plasticisation was found to be recoverable after desorption.

- Overall, UV radiation and moisture ingression were found to mitigate their effects, as one was leading to the development of surface hardness, while the other yielded its degradation. Additionally, UV radiation energy would be dissipating by removal of absorbed moisture, and thus not expended on the matrix post-curing or its subsequent photodegradation.

The primary underlying degradation mechanisms were determined for different types of GFRP composites as follows:

- Photodegradation of GFRPs and the subsequent material leaching were found as the chief cause of their rough surface after ageing, especially for those GFRPs with the chopped mat as reinforcement. Long-term exposure of GFRPs to UV radiation is known to increase the density of broken chains on the surface; then, the subsequent seasonal precipitations may leach the degraded chains and result in fibres blooming.

- For the chopped fibre reinforced GFRPs, bubbles and microcracks induced by weathering primarily led to the decline in flexural properties. Internal bubbles are
known to be expanded by ageing induced chemical reactions, as well as the microcracks which are developed by the internal stresses from UV radiation and the resultant density gradient in the material.

- For GFRPs with continuous fibres, the weathering induced decay at the interfacial bonds chiefly led to the decline in flexural properties. At the interfaces, Moisture ingression may lead to the differential swelling stresses, as different constituents may expand in different rates after moisture sorption. These internal stresses can degrade the bonding at fibre-matrix interfaces and result in their ultimate debonding during the long-term outdoor applications.

- The weathering induced decline in hardness was primarily attributed to matrix plasticisation, whose effect was deemed to be recoverable after desorption.

The effect of the studied design and process variables on the weathering performance of the material were found as follows:

- Among the studied design and process variables, the reinforcement architecture was determined as the most influential parameter for the weathering performance of final GFRP products, followed by our decision on applying a surface coating, and the selection of an appropriate initial curing condition.

- GFRP composites reinforced with woven fabrics demonstrated a better weathering performance than their chopped counterparts, either in their visual or structural properties. Their higher fibre content reduced the risk of matrix degradation although the decay at fibre-matrix bonding was still a serious structural concern in this category.

- Application of isophthalic resin as a surface coating was identified as an effective solution for limiting the photodegradation, and accordingly promoting the surface quality.
• Gel coat treatment was also helpful in stabilising the weathering induced variations in mechanical properties for the chopped fibre reinforced samples, as it effectively limited the matrix degradation and the resultant internal bubbles and microcracks.

• Gel coat treatment, however, was found to fail in restricting the weathering induced decay of bonding at the fibre-matrix interfaces and the subsequent interfacial debonding.

• Peeling of the applied gel coat from the material bulk was identified as another structural concern for the weathering performance of coated GFRPs, as water molecules may invade the resultant free volume, leading to the degradation of aged composites.

• Among the two curing states studied in this research, namely gradual cure in the ambient condition and rapid cure at an elevated temperature, the former was identified as a more desirable processing state to improve the weathering performance of GFRPs. Firstly, the structure of the matrix would be expected to become more brittle with the high level of DOC in composites cured rapidly in an industrial oven, posing the risk of interfacial debonding. Secondly, the reduced capability for moisture ingression in GFRPs with high DOC levels would mean their escalated risk of photodegradation.

Overall, the methodology used in this research was extremely helpful to systematically quantify and visualize the correlations existing between the climatic agents and changes in the material properties. The influence that a particular variable may exert on each category of observations was also effectively identified in this study. In other terms, PCA not only presented a detailed overview of correlations existing between variables, but also its visualisation capabilities helped us to gain a better insight into the causes and effects of degradation, under exposure to several climatic ageing factors.
5.2 Suggestions for Future Research

Since the current study was among the few that experimentally approached the natural ageing of composites over long-term exposure, there still remain potential research directions that could be pursued in the future, as follows:

- The chemical composition of the GFRP composites was not monitored quantitatively in this research during ageing. Fourier Transform Infrared Spectroscopy (FTIR), therefore, can be implemented as an applicable method to numerically track the weathering induced chemical changes.

- Fatigue has rarely been investigated in the literature for composites. More specifically, the effect of long-term outdoor exposure on the fatigue properties has barely been addressed. To fill this gap in the literature, weathering induced transition in the S-N diagram trends can be explored for FRP materials in order to detect how their fatigue strength may be affected by their long-term outdoor exposure.

- In this research, a numerical model was not derived from the experimentally gathered data. This model, derived from an extended dataset with more comprehensive measurements, can assist both designers and manufacturers in achieving a better prediction of the weathering trends and enhancing the long-term outdoor performance of their products.

- As the application of GFRP composites is widespread in the marine industry, similar research could be carried out on floating composite parts to investigate the effect of salinity, alkalinity, and acidity in the ocean/sea water. Determination of the seasonal transition in floating composite parts may also be beneficial to the boat manufacturers.
It should also be highlighted that there are many other factors involved in composites manufacturing, which were not studied in this research. As an illustration, apart from the hand lay-up process, other manufacturing processes, such as Resin Transfer Moulding (RTM) and Vacuum Assisted Resin Transfer Moulding (VARTM), can lead to variations in the long-term durability of products. The dust level in the factory environment may also be a critical factor in defining the weathering performance of products, together with the amount of silicone volatiles mostly found in release agents and vacuum bags. These agents can easily ventilate through the factory environment, sit on the laminas, and hinder the proper adhesion of laminas, resulting in the delamination of the laminated products. It is therefore deemed necessary to more attentively probe into how the weathering performance may be affected in FRRP materials by their manufacturing processes and the required processing environment. This may assist the future manufacturers in a better selection of the optimum processing condition in order to improve the weathering performance of final products.
References


