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Degradation mechanisms effect on the mechanical properties of pultruded CFRPS: a review

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Abstract

Environmental factors such as ultraviolet (UV) radiation, moisture, and temperature can promote degradation mechanisms in pultruded carbon fibre composites. It has been shown that UV radiation coupled with moisture accelerates chemical reactions, leading to molecular bond breakage and chalking, compromising the surface and the matrix. UV radiation and temperature have been shown to significantly impact durability when combined with mechanical loading. While some studies have provided valuable insights into the single degradation processes associated with UV radiation, moisture, and mechanical loading, a comprehensive understanding of their concurrent effects, particularly under conditions representative of open-field exposure, remains limited. This gap is largely attributed to key limitations in the existing body of research, including over generalised experimental protocols, a lack of standardised test methods for any simultaneous application, wide variability in material compositions and a predominant focus on single or sequential rather than simultaneous exposure scenarios. This review covers degradation mechanisms due to single, sequential and combined environmental effects with related testing approaches used to predict residual life. This review emphasises the need for a deeper understanding of the synergistic effects in the design and application of pultruded CFRP composite and for more realistic environmental conditions during testing to mimic real-world scenarios. In particular, the inclusion of mechanical loading within environmental chambers is essential for capturing the interactive effects of simultaneous environmental and mechanical stress.

Keywords CFRP, Pultrusion, Accelerated ageing, UV, Moisture

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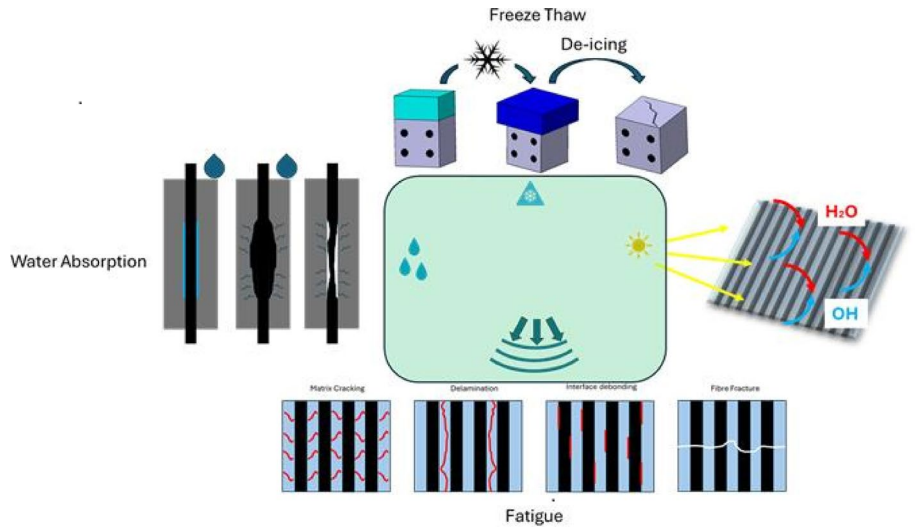
Graphical Abstract



1 Introduction

Pultrusion manufacturing is a highly efficient and rapid production method with rates of up to 5 m per minute [1], whilst still maintaining low manufacturing costs. This method involves pulling raw materials through a die, allowing for the extrusion of continuous and uniform cross-Sects. [1–3]. A typical pultrusion layout is illustrated in Fig. 1.

Pultruded composites represent a suitable material for transport and railway infrastructure, enabling the manufacturing of lightweight components, and unlocking greener and cost-effective electrification. However, there are several limitations, including challenges associated with controlling fibre content, resin distribution, and processing conditions. High resin viscosity is significantly influenced by flow effects and can lead to void formation, dry spots, and inconsistent thermal or curing profiles, reducing local load-bearing capacity and often causing property variations across a single component.

The inherent variability in the manufacturing process introduces significant uncertainty in estimating the long-term durability of pultruded composites under simultaneous environmental and mechanical loading [4]. Also, pultruded materials have been reported to demonstrate sensitivity to environmental factors, including temperature, moisture, and UV exposure [5, 6] which can affect their mechanical properties over time. The individual and synergistic effects that environmental conditions and mechanical loading have can result in accelerating the damage evolution [7, 8]. Different resin systems exhibit varying responses to environmental effects. Vinyl ester (VE) resin has been shown to be less susceptible to hydrolytic reactions than polyester (PE). Epoxy resins exhibit superior resistance to chemical degradation and mechanical wear compared to VE resins. However, it is often accompanied by a higher manufacturing cost [9].

When pultruded composites are subjected to both environmental and mechanical loading simultaneously, their mechanical performance can decline at a faster rate than when either mechanism occurs individually. Moisture-induced weakening of the interfacial bond, combined with mechanical stresses, can accelerate delamination propagation, which can lead to cracking in composites, facilitating the penetration of moisture and aggressive agents into the material. Such ingress can further accelerate the degradation

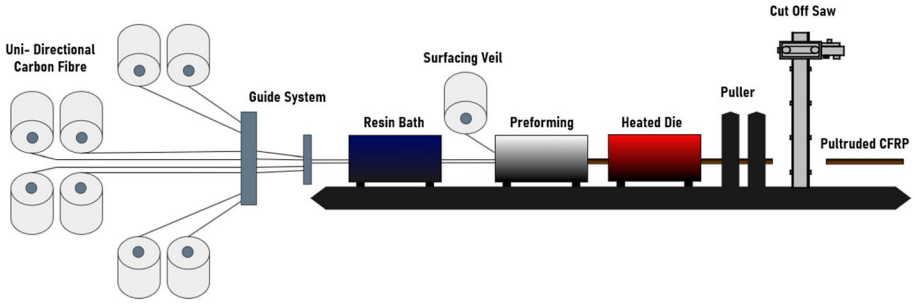


Fig. 1 - Pultrusion manufacturing Layout

processes [10]. This is particularly evident in the reduction of key mechanical properties, with tensile strength and interlaminar shear strength (ILSS) being among the most adversely affected, as reported in several studies [11, 12], although the magnitude of degradation varies depending on the exposure conditions and material systems examined.

The variation in the mechanical characteristics is commonly assessed through static tests carried out after the ageing process has occurred. Therefore, the effect of ageing is only measured in terms of residual strength available, rather than the real-time degradation promoted by the synergistic effect of these combined conditions [13, 14].

The objective of this review is to highlight avenues for further research on degradation mechanisms in pultruded carbon fibre reinforced polymers (CFRPs) associated with the synergistic effects of UV radiation, moisture and mechanical loading. Addressed first is UV exposure, which has the potential to significantly influence the composite's subsequent response to other degradation mechanisms such as moisture ingress and mechanical loading. The review is structured into 10 sections, with Sects. 2 to 7 focusing on individual degradation mechanisms, their associated experimental methodologies, and approaches to damage characterisation. Specifically, Sect. 2 addresses UV exposure, Sect. 3 examines moisture effects, Sect. 4 explores acidic and alkaline environments, Sect. 5 investigates the impacts of elevated temperatures, Sect. 6 covers the effects of freeze-thaw thaw and Sect. 7 discusses fatigue response. Section 8 covers current literature on the combined effects of the mechanism above, focusing on synergistic effects through simultaneous or sequential loading. Lastly, Sect. 9 concludes the key points of the mechanisms above, and Sect. 10 discusses the areas where further research is required to enable a deeper understanding of the synergistic effects.

2 Ultraviolet radiation

2.1 Single degradation mechanisms under UV

Exposure to UV radiation can induce physical and chemical changes, with degradation of the mechanical performance of polymers [15]. The effect of UV radiation on polymers is summarised in Fig. 2, showing a schematic representation of the degradation mechanisms including the initiation stage (generation of free radicals), propagation stage (series of reactions of radicals with polymer chains and generation of reactive chains), and termination stage (combination of radicals and active polymer chain that leads to non-reactive products) [25].

The photo initiator is excited by UV radiation at the desired frequency and intensity, which releases free radicals to extract labile hydrogen atoms from the polymer. After these free radicals react with oxygen in the air to generate hydroperoxides, they can

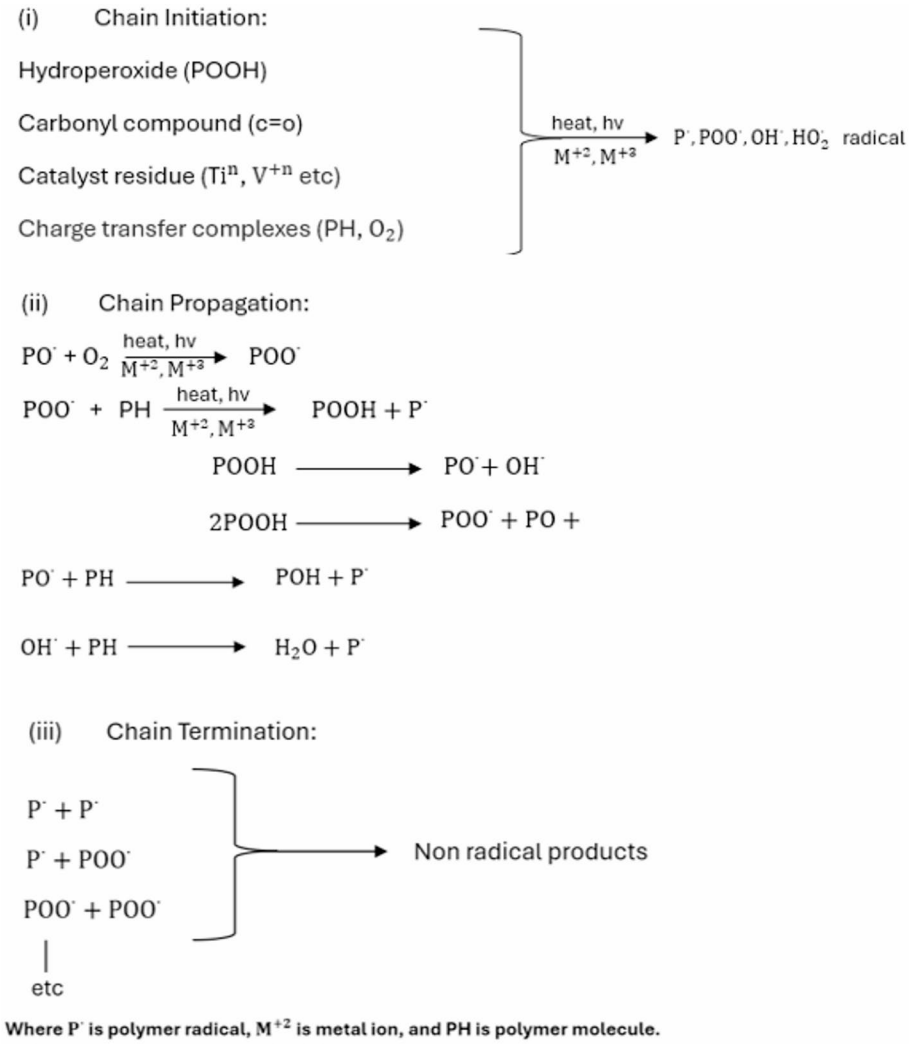


Fig. 2 General degradation mechanism of polymers due to UV exposure [16]

initiate a chain reaction to degrade the polymer matrix, causing crosslinking through a process known as radical-radical coupling. Continued chain scission causes a reduction in molecular weight, which in turn diminishes both the material's strength and heat resistance [17]. According to Lake-Thomas theory [18], as the chemical cross-linking density rises, the distance between cross-links decreases, resulting in a decrease in fracture toughness due to the reduced length of the polymer chains between the cross-links. The process of photo-degradation leads to embrittlement, surface cracking, discolouration, and a loss of transparency. Matrix-level surface oxidation might transpire, leading to the disruption of chemical bonds among molecules and influencing the material's surface gloss [19, 20]. In CFRPs, the oxidation behaviour of matrix polymers is heavily influenced by the geometry and ply orientation. Matrix oxidation is significant at both the exposed surface and the fibre-matrix interface and can progress through the thickness, greatly accelerating oxidative degradation when significant matrix cracking is present, exposing more surface [21]. Although UV-induced degradation is commonly described as being limited to a layer of approximately 10 μm underneath the surface [4] this depth can vary depending on factors such as ply orientation, and the intrinsic properties of

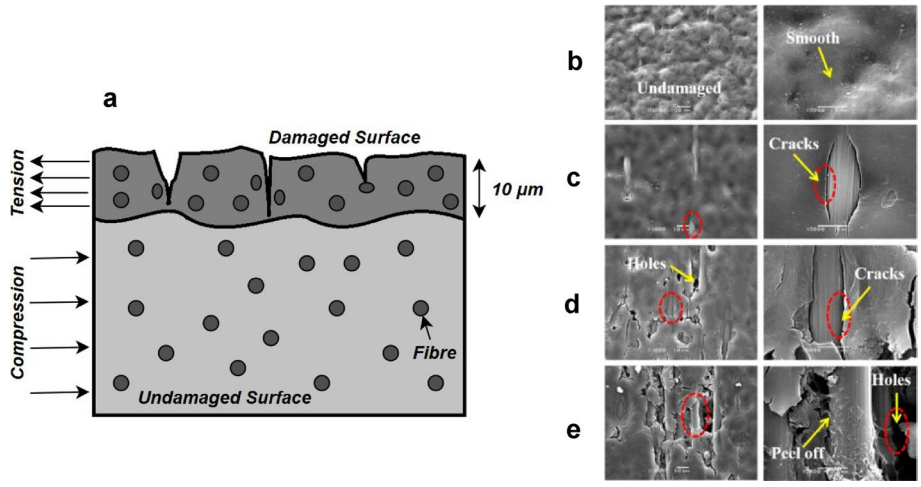


Fig. 3 **a** UV-induced layer-by-layer crack expansion mechanism, UV ageing of CFRP specimens between 0–80 days (surface microscopic morphology): **b** unaged; (**c**) 10 days; (**d**) 40 days; (**e**) 80 days [22]

the composite. Thermal expansion induced by the UV radiation has also been shown to affect the depth of UV deterioration, as it induces a residual stress field variable through the thickness (Fig. 3a [22]) that can further promote damage propagation and affect the mechanical properties, reducing the life of the structure.

Shi et al. [22] used Scanning Electron Microscopy (SEM) images to analyse UV degradation mechanisms in CFRP specimens at different UV ageing intervals, highlighting the progression of damage. Starting from the unaged condition (Fig. 3b), cracks can be observed after circa 10 days (Fig. 3c), which can propagate and combine with pitting and initial loss of surface material after 40 days (Fig. 3d). After 80 days, these damage mechanisms can spread, reaching fibres and producing matrix interface debonding (Fig. 3e).

Shi et al. [22] conducted tensile, compression, bending, ILSS and thermomechanical testing to monitor the degradation under UV ageing on fibre/epoxy composites prepreg manufactured through a wet lay-up process. The coefficients for the remaining strength model were determined based on data collected over an 80-day exposure period, and these values were used to extrapolate the projected residual strength after 800 days. Under longitudinal compression, residual strength was 1879 MPa, representing 51% of its original value under pristine conditions, while the flexural residual strength stood at 1322 MPa, or 77% of the initial strength under pristine conditions. These data showed a significant effect of the UV ageing on the residual strength. Fourier Transform Infrared Spectroscopy (FTIR) analysis combined with nanoindentation was used to both consolidate the degradation mechanisms and assess the severity of the brittleness effects associated with exposure to UV radiation.

Although photo stabilisers are effective in delaying the onset of UV-induced degradation in polymers, extended UV radiation exposure ultimately generates localised deterioration of the mechanical properties of the exposed surface [23, 24]. Another common solution extensively explored is the use of various protective coatings as a physical barrier between the material and the UV radiation [25, 26]. To mitigate the effects of UV ageing, various strategies have been employed, including encapsulation of the materials, which can provide a sealed environment that isolates the material from the external environment [27].

2.2 Damage characterisation under UV

The methods of accelerated ageing utilise radiation emitted by various light sources as a catalyst. Instances of these sources include carbon arc, mercury, metal halide, xenon and fluorescent tube lights, among others [14, 28, 29]. When determining appropriate testing procedures for applying UV radiation to CFRP samples, the international standards ISO-4892 and ASTM-D4329, applicable to plastics, are typically used since the main degradation occurs in the matrix. Effects like natural sunlight exposure can be replicated in the test using mirrors that can be utilised to both amplify solar radiation and track movement throughout the day.

Several studies have investigated the reproducibility of solar radiation. Filtered xenon light sources, which emit light in the 290–400 nm range [30] or UV-A fluorescent lamps characterised by peak emission at 340 nm, are typically suggested for replicating the detrimental impacts of solar radiation on many plastics. The UV-A source closely mimics the radiation typical of a midsummer noon within the spectral range of 320–400 nm, but doesn't account for environmental variables such as atmospheric scattering and pollution, which can affect the transmission and intensity of UV radiation [31]. It is worth noting that UVA radiations, along with a limited amount of UVB (280–315 nm), constitute the only portions of the light spectrum that reach the Earth's surface (Fig. 4). This distribution is due to the filtering effect of the ozone layer, which blocks UVC wavelengths falling within the range of 200–290 nm and a substantial portion of UVB (70–90%) [32]. Humidity, rainfall, wind direction and velocity, cloudless exposure duration, geographic latitude, and the angle of incidence of UV radiation on the exposed surface collectively influence the intensity and duration of UV radiation interacting with the material. These factors determine the extent of UV exposure and its effects on the material's surface properties.

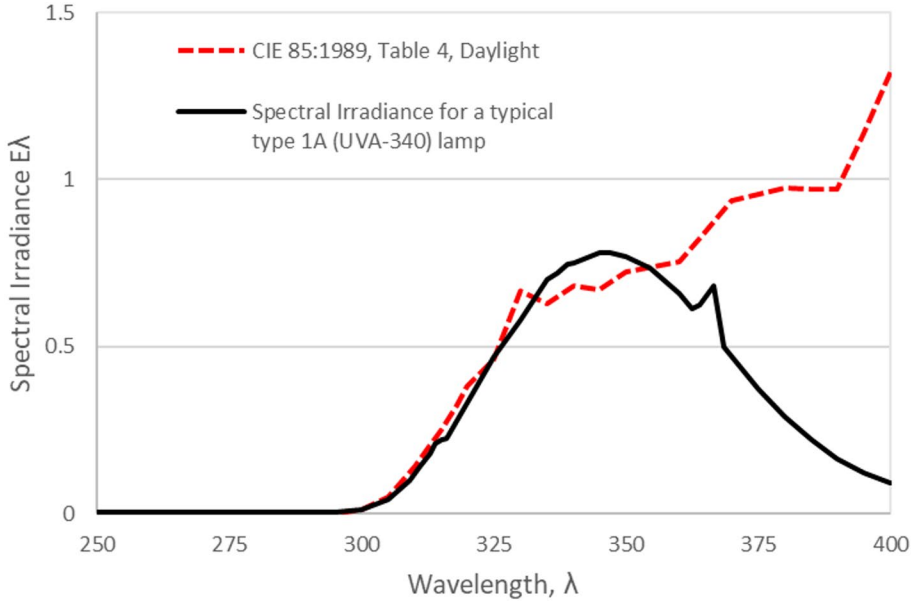


Fig. 4 Spectral irradiance for a typical UVA −340 lamp compared to CIE No. 85:1989 Global Solar Radiation [33]

3 Effect of moisture

3.1 Degradation mechanisms

Exposure to water can occur due to numerous sources, rainfall being the primary natural cause, but also dew/condensation and/or environmental humidity in areas of close proximity to natural water bodies. Exposure to water or high levels of moisture has the potential to damage fibres, matrix, and the fibre-matrix interfaces. However, inorganic fibres like carbon or glass do not absorb water [34, 35]. The primary entity that facilitates water ingress from the surroundings is the resin matrix. Water enters the resin matrix primarily through two mechanisms: diffusion, where water molecules spread across the material, and capillary action, which draws water into the matrix via small voids or pores [36].

Water absorption behaviour in polymers is linked to their inherent hydrophilic properties and the polarity of the polymer chains. Initially, the rate of water absorption is high, with most alterations occurring within the first three days as water diffuses from the outer surface. The absorption rate gradually decreases, as it must pass through a progressively thicker layer of polymer that is saturated with water, which leads to a reduction in the diffusion rate over time [9].

It is essential to recognise that the extent of deterioration varies between distinct resins, including epoxy, PE, and VER, with unsaturated PE resin being notably the most susceptible to water due to its PE linkages [37]. The smaller number of open sites in the chain structure of VE enhances its resistance to hydrolysis under water exposure and minimises the likelihood of osmotic bubble formation [38].

The water absorbed by the matrix induces volumetric changes that result in microcracks with detrimental effects on the mechanical strength [39].

Water uptake results in both reversible and irreversible physical and chemical damage, namely, plasticization and hydrolysis [40]. Plasticization occurs when a penetrant is absorbed into the polymer matrix, causing the membranous structure of the polymer to swell. The occurrence of this phenomenon can lower the glass transition temperature (Tg) and reduce the stiffness of fibre-reinforced polymers (FRPs). In the case of a typical PE resin, a 2% moisture weight increase causes Tg to decrease by about 15–20 °C [41]. This is also accompanied by a decrease in ILSS and flexural properties [42]. As degradation progresses, fibre-dominated properties like tensile strength remain relatively stable, while matrix- and interface-dependent properties, such as flexural and shear strength, experience considerable deterioration [43, 44]. Water ingress at the fibre-matrix interface can induce additional expansion, facilitating the growth of microcracks [45]. Due to this phenomenon, the FRP material can absorb even more water. Moreover, the separation between fibres and the matrix can arise, potentially causing parts of the matrix material to dissolve hydrolytically in water and leach out along the interface [46]. Dissolution and swelling at the fibre-matrix interface have been observed to impair the bond, leading to a diminished ILSS of the FRP material. According to Zhang and Mason [47] in terms of ILSS after only 30 days of immersion, UD CFRP with epoxy-based matrix decreased by 6.3% when immersed in water and 10% when immersed in seawater at room temperature (RT).

Bin Hong et al. [48] studied the performance of pultruded CFRP plates made from an oligomeric prepolymer diglycidyl ether bisphenol-A (DGEBA) epoxy matrix. While carbon fibres themselves do not absorb water, it was observed that at temperatures between

20 and 60 °C the CFRP plates exhibited a higher maximum water uptake (M∞) than the neat resin matrix. At 60 °C, the neat epoxy resin M∞ was 0.53%, whereas CFRP plates exhibited an M∞ value of 0.77%. The author attributed this to the wicking effect due to fibre debonding. As the fibre–resin adhesion deterioration rate corresponded to an increased temperature.

For CFRP plates, the presence of fibres inherently modifies the diffusion pathways, and when defects such as microcracks or voids are present, they act as channels that enable water molecules to migrate along the fibre surfaces without requiring significant energy to penetrate the dense polymer matrix. The lower activation energy (Ea) observed for the CFRP plates shows that water molecules are more readily absorbed, which accelerates water ingression and enhances the severity of degradation mechanisms.

While plasticisation is somewhat reversible upon drying, allowing for the potential recovery of mechanical properties [49], in contrast, hydrolysis results in the rupture of polymer chains, weakening the molecular bonds and subsequently reducing the overall bonding strength between the molecules [50, 51]. "Wet-Dry Cycling" is a test protocol that allows drying periods between water ingression. Frequent cycles of water absorption and desorption cause the matrix to repeatedly swell and shrink, generating stress at the fibre-matrix interface. This cyclic stress causes fibre-matrix detachment and a decrease in fibre-matrix adhesion [52]. Hong et al. [53] investigated pultruded CFRP plates with PAN-based carbon fibres in epoxy resin under the combined effects of seawater for 1 year on the in-plane shear strength (IPSS). Different temperatures (20 °C, 40 °C and 60 °C) and retentions of 89.4%, 92.3% and 87.9% were observed, respectively. Once dried, the reversible effect of plasticization was identified on the samples, since the retention percentage of IPSS returned to 92.8%, 98.9% and 96.8%. The slight decrease has been explained by the irreversible deterioration of the interfacial bond strength due to micro-cracks caused by the cycles of water absorption and desorption, causing the matrix to repeatedly swell and shrink.

Sealants, barrier films [54] and coatings with hydrophobic properties can contribute to reducing moisture absorption in CFRP composites [55], creating a barrier against moisture ingress that also possesses chemical resistance to environmental factors [56]. The need for regular re-application must be considered, as protective coatings and sealants are prone to wear and cracking under environmental effects and mechanical loading. Surface functionalization has been proposed to enhance weakened fibre-matrix interfaces due to dissolution and swelling. Silane coupling agents are likely to produce reactive sites that bond with the matrix resin, improving interfacial adhesion. Greater contact can lead to enhanced mechanical performance, including ILSS [57], through better stress distribution. The enhanced adhesion not only affects the mechanical properties but also the thermal and chemical stability of the composites [58]. Additionally, by fluorinating the carbon fibre sizing, a hydrophobic behaviour can be imparted to the fibres. The fluorination of the sizing promotes controlled etching of the sizing layer, which reduces the dispersive component of the fibre surface energy, potentially enhancing bonding by preventing moisture absorption at the fibre/matrix interface. This process ensures the retention of strong adhesion between the reinforcement and the matrix [59].

3.2 Experimental approach

There are multiple approaches to investigating the absorption mechanisms and the effects on the mechanical properties. Extensive literature would indicate three main methods to expose samples to moisture/water: liquid immersion [39, 55, 60], condensation [5] and water spray [13]. While no off-the-shelf "commercial products" are specifically marketed for CFRP water immersion tests, manufacturers including PolyScience USA and Julabo UK are both suppliers which offer water baths with precise temperature control. Alternatively, to simulate rain or spray environments, QUV accelerated weathering testers manufactured by Q-LAB, Ohio, USA, have the capability to simulate dew and rain with condensing humidity and/or water spray at controlled, elevated temperatures. The ASTM-D5229 standard outlines guidelines to standardise testing methods for evaluating moisture absorption properties and the attainment of equilibrium conditions in polymer matrix composites, ensuring reliable and comparable results. In general, a reinforced polymer matrix composite tested below its Tg follows the single-phase Fickian diffusion model. However, some compositions of CFRP, like those with a toughened epoxy, require the use of a dual-phase moisture absorption model [61]. Therefore, these limitations must be considered when utilising this model. To ensure reliable and reproducible test results, it is crucial to consistently monitor both moisture content and desired mechanical properties. The strength retention of either tensile [62, 63], shear [63] or flexural modulus [64] at regular intervals throughout the exposure period is commonly used to monitor the degradation process. However, when accelerated ageing protocols are employed, even with strict adherence to standardised procedures, the resulting data may not fully capture the long-term degradation mechanisms that occur under actual service conditions. Therefore, it is common practice to compare accelerated ageing results with real-time environmental exposure data to establish meaningful correlations and validate the applicability of accelerated testing methods.

4 Effect of acidic and alkaline environments

4.1 Degradation mechanisms

Depending on the application, CFRP may be required to withstand exposure to chemically aggressive environments, including alkaline and acidic conditions resulting from sea salts in humid climates, acid rain in densely populated urban areas, and de-icing salts commonly used in cold regions.

In aqueous environments, CFRP materials may be susceptible to microbial colonisation and degradation. Alkaline and acidic solutions have the potential to induce degradation in CFRP materials in a manner similar to water immersion, with both types of solutions able to infiltrate the material through diffusion, causing expansion of the matrix and delamination at the fibre-matrix interface.

Schematic representation of degradation mechanisms of the ester bond under acidic and alkaline solutions is presented in Fig. 5.

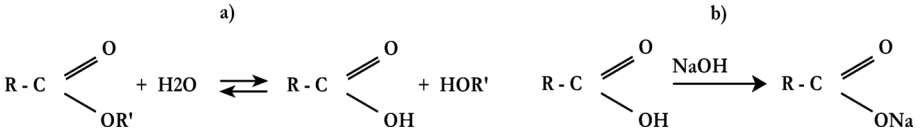


Fig. 5 Reaction mechanism of degradation of ester groups in (**a**) acidic and (**b**) alkaline solutions [65]

Investigations into the effects of hydrochloric acid (HCl) and sodium hydroxide (NaOH) on the mechanical properties of epoxy composite laminates revealed that NaOH exposure led to decreases in flexural strength of approximately 5.8%, 11.1%, and 22% after 12, 24, and 36 days, respectively. In comparison, HCl exposure resulted in decreases of 2.9%, 9.0%, and 16.2% under the same conditions. These results indicate that alkaline solutions tend to produce a more aggressive degradation with epoxy composite laminates, leading to a greater decrease in the flexural properties [66]. These findings have been confirmed by other studies reporting results from three-point bending and flexural fatigue testing [67]. However, it is important to note that these findings have been generated with different materials, layup and testing protocols and the extent of degradation may vary depending on factors such as resin type and duration of exposure. Although limited, research into pultruded CFRP specimens exists [55, 68, 69] most of the extensive work has been done around specifically epoxy, PE and VE resin [70, 71] which are susceptible to an acidic/alkaline-induced degradation mechanism. PE-based materials tend to display lower physical and chemical stability in alkaline solutions compared to vinyl-ester based materials. VE resins have low polar groups on the chemical backbone and are more resistant to hydrolysis compared to PE resins [72]. Acidic exposure, characterised by greater surface roughness, crack development, and sulphur diffusion into the cracks, has been shown to affect PE resin more severely than bisphenol-A-based epoxy vinyl ester resin [71].

The permeation of chloride ions into the epoxy resin matrix facilitates the hydrolysis reaction, which in turn compromises the mechanical integrity of the specimen [36, 68]. A typical alkaline solution, which is commonly investigated through research, is artificial seawater. As salt particles accumulate on the surface, they can obstruct continued water absorption, while the resulting osmotic pressure works against the process of water uptake.

Feng P [73]. studied the degradation behaviour of epoxy-based glass fibre-reinforced polymer (GFRP) composites when exposed to sulfuric acid solution. The research observed phenomena such as debonding, delamination, and crack propagation in the presence of sulfuric acid solution. The epoxy-based GFRP specimens, after being immersed for 90 days in a 30% sulfuric acid solution, exhibited a reduction in flexural strength and modulus, which decreased to 66% and 63% of their initial values, respectively. In contrast, pultruded GFRP plates exhibited robust resistance to saturated sodium chloride (NaCl) solution, with minimal impact on their mechanical properties, hardness, appearance, and weight. Whereas, in the context of CFRP, Lu et al. [74] observed that pre-stressed CFRP sheets in a chloride-containing environment at room temperature did not notably affect the CFRP strain-to-ultimate strain ratio (utilisation ratio) when used to strengthen reinforced concrete beams. And the strengthening effectiveness was found to enhance as the applied load increased.

Since alkaline and acidic degradation testing are like moisture testing procedures, prevention methods of this type of degradation are also of a similar nature. Matrix composition and its resistance to alkaline/acid attacks [75, 76] is crucial to investigating mitigation, including surface coatings and sealants [56]. Epoxy resins, which are frequently used with CFRP, can have their corrosion-resistant properties further enhanced through improved bonding by incorporating inorganic compounds and carbon-based materials [76]. For acidic mitigation, inert filler materials can be incorporated in the

matrix to dilute the effects of acid exposure and reduce chemical reactivity [77]. Acid scavengers are essential in the polymer industry, as they deactivate catalyst residues, predominantly chlorides, to prevent unwanted reactions and protect the polymer [78].

4.2 Experimental approach

Alkaline and acidic degradation mechanisms are assessed using immersion testing procedures that are similar to moisture but use altered liquid mediums, adjusted to the specific pH required to match the natural environment/conditions. By doing so, the chemical interactions and degradation mechanisms that occur when polymers are exposed to alkaline or acidic substances can be simulated. A typical medium investigated throughout literature is seawater [53, 72, 79, 80]. The standard procedure for preparing substitute water is defined by ASTM D1141-98 or comparable standards to ensure consistency and accuracy. While laboratory experiments commonly employ distilled water as a standard testing medium due to its neutral pH and absence of impurities, these characteristics make distilled water an ideal baseline medium to isolate and study specific variables without interference from extraneous factors. However, this very advantage also introduces a limitation when attempting to extrapolate laboratory findings to real-world scenarios. For instance, when evaluating the corrosion resistance of GFRP in outdoor settings, it's essential to consider exposure to rainwater, which often contains dissolved atmospheric gases and pollutants, leading to a slightly acidic pH. The acidic nature of rainwater can influence the degradation behaviour of materials over time, potentially affecting their mechanical properties and structural integrity [81].

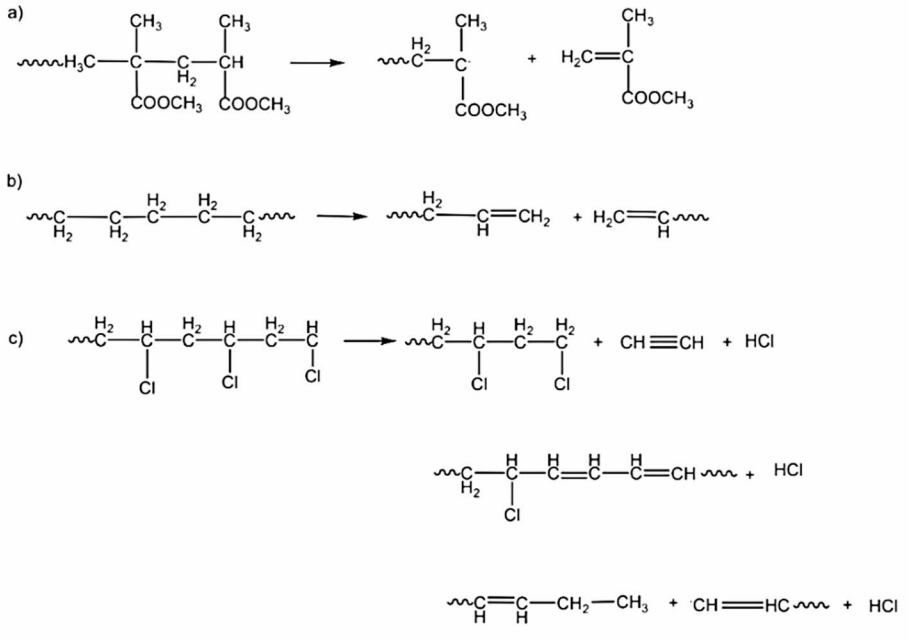


Fig. 6 Thermal degradation mechanisms of polymers: **a** Depolymerisation (e.g. PMMA), **b** Random chain scission (e.g. PE), and **c** Side group elimination (e.g. PVC) [84]

5 High temperature

5.1 Degradation mechanisms

In structural applications, the exposure of CFRP to elevated temperatures (temperatures above room temperature) may manifest due to various factors, including proximity to heat sources, instances of friction, or localised environmental conditions. In addition to this, solar radiation represents a noteworthy contributor to this thermal exposure, inducing heightened surface temperatures, particularly in regions characterised by intense sunlight and prolonged exposure periods. Thermal degradation of polymers has been extensively studied [82, 83] and three main reaction mechanisms, reported in Fig. 6, have been identified, namely depolymerisation (separation into monomers), random chain scission (fragmentation of polymer chain into smaller parts), and side-group elimination (separation of a side group from the main polymer chain) [84].

To avoid inducing alterations that would not occur under typical environmental conditions, ageing processes need to be carried out at temperatures lower than the Tg. However, short-term exposure to temperatures above Tg has been found to offer additional post-curing effect with a minor improvement in material strength [85]. However, the improvement depends on the initial degree of curing of the resin and the duration of the exposure. As the ambient temperature reaches Tg, the matrix stiffness decreases, compromising the fibre-matrix interface, with the matrix becoming less capable of effectively transferring stress. This weakening leads to shifts in stress distribution within the composite, ultimately affecting its load-bearing capacity [86]. A wide range of research efforts have been devoted to studying the thermomechanical behaviour of CFRP, examining how these materials perform under the combined influence of thermal cycling and mechanical loads [85–87]. E.J. Bosze [88] investigated the properties of two materials made from hybrid carbon/glass epoxy pultruded rods. The study unveiled the effects of the glass transition temperature and variation in composition on the strength retention. It was observed that the composite with lower Tg (176 °C) retained its tensile strength only up to 80 °C while the composite with higher Tg (202 °C), demonstrated remarkable resilience by maintaining its tensile strength until 170 °C. Matrix softening and the weakening of the fibre-matrix bond are the key contributors to strength loss at elevated temperatures, with a clear relationship between the temperature dependencies of the storage modulus and tensile strength in unidirectional composite.

At high temperatures, both the polymer matrices and the fibre/matrix interfaces can undergo deterioration, even in environments devoid of oxygen. As a result of thermal degradation, fibre-matrix debonding and transverse microcracks cause stress concentration at the interface due to mismatched stiffness and differences in the coefficients of thermal expansion. Microcracks lead to an increase in exposed surface area and the creation of additional oxygen diffusion pathways, which can accelerate the oxidation process, increasing exponentially the rate of degradation [89]. Muna et al. [90] studied how thermal exposure influences the mechanical performance of unidirectional CFRP composites. They observed a decline in both mechanical strength and Young's modulus. This degradation becomes evident when exposed to cyclic temperature variations oscillating between 50 °C and 70 °C. Upon exposure to thermal cycling, the specimens demonstrated a loss in mechanical performance, with tensile strength reduced by 9.6% and elastic modulus decreasing by 26.5%.

5.2 Experimental approach

Previous approaches for testing the high-temperature applicability of CFRP involve exposure to high-temperature conditions through either heat flux [91] or temperature control [92]. These methods use variables such as heating rates, dwell times, and peak temperatures to accurately simulate the required thermal stress scenarios.

Traditional approaches in the field often rely on high-temperature furnaces due to their versatility, precision, and ability to create controlled thermal environments [87, 92]. Other approaches employ an induced radiant heat flux source, utilising mechanisms such as infrared radiation or induction heating, which offer advantages in terms of targeted and controlled heating. Another approach described in the ASTM- E1952-23 uses modulated temperature differential scanning calorimetry (MT-DSC) for the indirect characterisation of thermal conductivity and thermal diffusivity. By employing MT-DSC, researchers can gain valuable insights into the thermal behaviour of materials without directly measuring these properties, offering a non-destructive and efficient means of assessing thermal performance. However, MT-DSC operates on a very small scale, often analysing samples weighing in milligrams, which will not be fully representative of the thermal behaviour exhibited by larger structural components. For instance, DSC may not adequately capture the heat distribution and thermal gradients that would occur during the operation of a large composite structure. There are facilities, such as the Fast Blade facility at the University of Edinburgh, that can perform fatigue testing on large-scale composite structures without temperature control, providing a more complete picture of material performance under realistic operating conditions. The combination of both small-scale thermal assessments and large-scale mechanical evaluations could offer a comprehensive understanding of material behaviour under thermal loading. Currently, after the material has undergone thermal conditioning, assessing at predetermined time intervals the residual mechanical properties in terms of variation in tensile strength [93], compressive strength [94] and flexural strength [95] provides quantifiable data on the strength and overall performance of materials post-exposure. Although useful, it primarily yields results that represent the material's state after the thermal exposure has ceased and does not capture dynamic changes during exposure.

6 Freeze thaw

6.1 Degradation mechanisms

At low temperatures (below 0℃) and during freeze-thaw cycles, the flexural stiffness of FRP materials has been shown to increase, primarily due to the stiffening effect of the resin matrix at these lower temperatures. Focusing on dry states responses, Aniskevich et al. [96] investigated the freeze-thaw cycling effects on GFRP materials in both dry and wet conditions. The study found that, for the dry state, freeze-thaw cycling had little to no impact on the flexural modulus, strength, thermal expansion coefficients, and glass transition characteristics of the material, with even a slight increase of flexural modulus. Similar findings by Grammatikos et al. [97] showed that the dry state and wet state of GFRP throughout freeze–thaw cycling produces negligible change in tensile modulus with a small upward trend observed in the tensile strength of dry state samples. Although this is not a consistent observation, in the case of freeze-thaw, the type of cycling, the duration of each cycle, and the order of exposure are the most important factors affecting the material degradation. Shi et al. [98] compared the performance of CFRP and

GFRP samples exposed to 200 freeze-thaw cycles between −17° and 8℃, and, once the samples were dried, a reduction in the tensile strength of 12% and 14%, for CFRP and GFRP respectively, was observed. GFRP [99] cycled in a wet state shows a significant degradation of the tensile strength due to plasticisation, although if the soaked material is left to dry, it recovers its initial mechanical properties. The slight decline in mechanical performance is due to the irreversible damage caused by the expansion of frozen water within cracks and voids, leading to debonding and the propagation of transverse microcracks [97]. Li et al. [100] compared the effects of freeze-thaw on GFRPs, CFRPs, and Basalt Fibre Reinforced Polymers (BFRPs), and although after 90 freeze-thaw cycles, GFRPs and BFRPs showed a negligible change in tensile properties, CFRP showed a significant reduction in elastic modulus and strength, 16% and 18% respectively. The difference was attributed to CFRPs exhibiting a significant mismatch in the coefficients of thermal expansion (CTEs) between the fibre and matrix, which can induce microcracks in the resin around the fibres during cycling, thus causing debonding of fibres from the matrix.

6.2 Experimental approach

Testing the freeze-thaw (F-T) applicability of CFRP composites involves subjecting the material to cyclic freezing and thawing conditions to simulate real-world exposure in cold climates. Traditional freeze-thaw tests use programmable environmental chambers. Manufacturers like Thermotron have commercially available chambers that can simulate different temperature cycles. The ranges of temperature used are typically between −20 °C and +20 °C [101]. It is important to note that certain applications necessitate the simulation of more extreme environmental conditions, and in some extreme applications, temperatures have been tested at ranges from −60 °C to +50 °C [102]. Each cycle typically lasts between 4 and 8 h, with freezing and thawing phases of equal length, applied for a total of 90–300 cycles [100, 103]. To obtain reproducible results for F-T cycling on pultruded FRPs, the ASTM D7792 Standard [104] can be used, which prescribes 100 freeze-thaw cycles followed by mechanical testing for the evaluation of residual strength, similar to those used for moisture absorption. However, it's important to stress the limitations that when accelerated ageing protocols are employed, due to their unrealistic conditions, even with strict adherence to standardised procedures, the resulting data may not fully capture the long-term degradation mechanisms that occur under actual service conditions.

7 Fatigue response

Although limited literature exists on the fatigue response of pultruded CFRP, insights can be drawn from other pultruded fibre-reinforced polymer (FRP) systems with similar matrices [105]. Typical damage mechanisms associated with fatigue failure of the FRPs include delamination, matrix cracking, fibre-matrix debonding, void growth and fibre breakage [106–108]. It has also been observed with high fibre volume fraction pultruded CFRPs that fibre bridging and pull-out can occur [109]. In pultrusion, composites are produced with fibres that are not perfectly aligned and uniformly distributed in the cross-Sect. [110]. The presence of voids, weakly bonded spots and the strength of the fibre-matrix interface [111] can affect the strain distribution and ultimately the fatigue strength. Pultrusion is characterised by high fibre content, which enables high

modulus in the fibre direction but can promote fatigue damage at the matrix interface, due to the difference in strain level when externally loaded. While it is generally accepted that higher fibre volume fractions can enhance the mechanical properties of CFRPs, including their fatigue resistance [112], there is a trade-off as the likelihood for internal stress concentrations to accumulate increases [113]. Although fibre content plays a major role in fatigue limit, it is still dominated by the damage developed in the matrix. The fatigue mechanism in FRPs is strongly affected by frequency [114], and the stress ratio of the applied load [112, 115]. CFRP specimens, tested under low and high cycle fatigue, develop damage in the form of transverse crack propagation and delamination [114] In the fibre-dominated direction, higher stresses can cause fibre fracture or progressive interface separation [116]. In the transverse or off-axis directions, at the fibre-matrix interface, stress concentrations due to mismatch in the orthotropic properties can induce matrix cracking and delamination [117].

During high-cycle fatigue, heat dissipation plays a critical role in modifying the failure mechanisms of CFRPs. The generation of heat primarily arises from two key sources. The first is internal friction, which is largely a result of the viscoelastic behaviour of the polymer matrix. When subjected to mechanical stress, the polymer chains undergo deformation and relaxation, which dissipates energy as heat. This viscoelastic relaxation is influenced by factors such as temperature and the rate of applied stress. As the temperature rises, the mobility of the polymer chains increases, enhancing the relaxation processes and consequently leading to greater heat production [118]. The second source is frictional heat, which is generated from various microstructural interactions, like relative motion between cracked surfaces and sliding or debonding at fibre-matrix interfaces [119]. Both mechanisms can produce a rise in temperature with localised heat that affects the strength of the interface between fibres and matrix and, in turn, softens the matrix, reducing the effectiveness of the stress transfer between the fibres and matrix with extended damage [114]. To avoid self-heating in FRP, the common approach reported in literature is to apply the cyclic loading at a frequency no greater than 4 Hz [110]. Lower frequencies are used as localised heating isn't a concern, the heat is dissipated into the surrounding environment. The internal temperature in the specimen must not exceed + 10 °C, according to ISO 13003:2003 [120]. Previous studies on the effects of frequency and internal temperature rise in GFRP have explored using broader frequency ranges and found that testing at 8 Hz only showed self-heating of approximately 1 °C [105]. Understanding the interplay between the aforementioned factors and environmental conditions is crucial for civil and rail applications. This necessitates an in-depth examination of how materials behave under combined loading and environmental influences. Future chapters will build on this foundation by examining the synergistic effects reported in the literature, offering valuable perspectives on the effects on material performance.

8 Combined degradation mechanisms

8.1 Elevated temperature and mechanical load

There are several studies on the combined effects of temperatures and mechanical load on CFRP [87, 90, 121, 122]. It has been proven that sustained mechanical load and high temperature accelerate creep damage [123]. Zhou et [87] examined CFRP tendons under these conditions and found a significant reduction in both strength and elastic modulus

as the temperature increased. At a critical strain of 0.012, it was observed that tendons subjected to a temperature of 20 °C could withstand up to 2 GPa before failure. However, this performance deteriorated significantly when subjected to higher temperatures, dropping to 1 GPa when the temperature was approaching 200 °C, indicating a substantial loss in structural integrity.

Mechanical loads at elevated temperatures can induce stress concentrations in regions where the material is weakened by thermal degradation or interfacial debonding. These stress concentrations become focal points for crack initiation and propagation, potentially leading to delamination [124]. Nguyen et al. [125] observed similar degradation in the tensile properties of CFRP exposed to high temperatures. At 240 °C, the tensile strength decreased by approximately 50%, and at 600 °C, it decreased by almost 90%. Showing that the ultimate strength of CFRP is significantly vulnerable to temperature increases.

Wang et al. [93] carried out a comparable study on the effects of elevated temperatures on the structural behaviour of Sika CarboDur 1214 pultruded plates bonded with epoxy resin. Their study covers the failure modes coupling temperature and mechanical loading, identifying four temperature-dependent stages designated as Modes I -IV.

Mode I with temperature values ranging between 22 °C and 50 °C, the temperature showed no change to the failure mode, and specimens failed in a brittle fibre rupture fashion. Mode II with temperature values ranging between 150 °C and 450 °C, there was a gradual reduction in ultimate tensile strength (UTS), with reductions of up to 40% at temperatures up to 200 °C and approximately 50% at 300 °C.

The last two modes, Mode III (450 –706 °C) and Mode IV (above 706 °C), observed a complete loss of epoxy matrix and considerable oxidation of the carbon fibres. Consequently, at higher temperatures, the primary failure mode of FRP materials shifts from being matrix-dominant to also being governed by the fibres.

In the context of fatigue, Mosallam et al. [126] examined the impact of thermal cycling on the fatigue life of CFRP composite laminates. The samples underwent 50 cycles between − 33 °C and 71 °C under a pre-tension of 30% of their ultimate tensile load. Although Tg was not reached, the results demonstrated a significant reduction in fatigue life compared to unconditioned specimens at the same stress level, with the fatigue life decreasing from 10^6 cycles to only 9.6×10^3 cycles.

8.2 UV and water/high moisture

Research into the environmental degradation of CFRP due to the combined effects of UV exposure and moisture is a well-explored topic. However, the findings are often contradictory. Some studies indicate that CFRP is highly susceptible to these degradation mechanisms [127], while others suggest that the conditioning process is insufficient to cause significant degradation [14]. These discrepancies stem from differences in material configurations and testing methodologies, particularly whether the exposure is conducted sequentially or simultaneously. Most studies tend to use sequential exposure, with cycles of UV radiation and condensation occurring every three hours [127].

In a study conducted by Lu et al. [15], a series of accelerated weathering tests was undertaken, subjecting Polyvinyl chloride (PVC) and unidirectional E-Glass corrosion Resistant (E-CR Glass) specimens to 1000 h of exposure, with an irradiance level of 1.5 W/m² at a wavelength of 340 nm. Surface roughness analysis revealed that the

average roughness of epoxy specimens underwent a reduction of 12.5%, following the 1000-hour UV exposure period. The statistical disparity between the roughness data collected before and after UV exposure pointed towards a UV-induced planarization effect on the material surfaces.

Furthermore, it was also observed a change in thickness with 9.4 ± 1.7 mm in epoxy specimens after the same duration of UV exposure. The study suggested that it might partly be attributed to the particle removal mechanisms [7, 128].

The particle removal effect arises when water infiltrates voids and microstructural defects generated by UV-induced photo-degradation. Under conditions of slow water flow or moisture ingress, these surface defects facilitate the detachment and transport of polymer fragments. The mechanical action of water, combined with the reduced cohesive strength of the degraded material, enables the removal of surface particles. This process exposes underlying, less-degraded polymer layers to continued ultraviolet radiation. It has also been observed that the increased absorption rate from the heating of water molecules through irradiation directly influenced the void growth rate and subsequently increased the rate of internal water pressures in the filled voids.

Kumar et al. [5], highlighted the significant impact of synergistic interactions between UV radiation and condensation in CFRP. The study concluded that the combined exposure to these factors results in a range of detrimental effects, including increased matrix erosion, microcracking, fibre debonding, fibre loss, and void formation with a substantial decline in transverse tensile strength. When subjected to only 500 h of UV the reduction was only 9%. Over a span of 1000 h of cyclic exposure to UV radiation and condensation resulted in a 29% reduction in transverse tensile strength, and a significant reduction in the transverse modulus.

Laís Vasconcelos da Silva et al. investigated the ageing effect on both tensile behaviour [13] and short-beam strength (SBS) [14] on VE/epoxy resins subjected to UV and immersion/water spray. UV radiation plus water-spray ageing resulted in negligible effects on the tensile strength and modulus with no mass loss observed. The same observation was made for the SBS values on either VE or epoxy. The authors concluded that the conditioning method is ineffective in inducing considerable degradation to the bulk of the samples.

8.3 UV and elevated temperature

The interaction known as synergistic effects occurs when high temperatures and UV radiation act in tandem, resulting in an accelerated degradation of CFRPs due to the collective influence of these factors. Whilst UV radiations primarily contribute to surface damage and discolouration, it is expected that when combined with high temperature, it would increase the rate of thermal expansion and contraction, increase the rate of chemical reactions, intensify the oxidative processes and thus, increase the degradation mechanisms. The process of accelerated oxidation occurs when elevated temperatures expedite the photo-oxidation process and other catalysts (or both) triggered initially by UV radiation [129]. Liau et al. [130] found that UV radiation can initiate microcracks, which can propagate once subjected to thermal shock. Although, Nguyen PL et al. [131] explored the impact of 774 h of UV and/or heat exposure on carbon fibre and CFRP specimens and found that neither the 40 °C temperature nor UV exposure had any significant effect on the elastic modulus or tensile strength of the CF and CFRP specimens,

despite differences in the thickness and number of carbon fibre layers. Ayman Mosallam et al. [126] studied the effects of UV and heat on the fatigue strength at different stress ranges, showing a 5% reduction in fatigue life for CFRP specimens exposed to UV radiation alone, but when coupled with temperature, further reductions (8%) were observed. This also could be due to the thermal stress arising from the thermal expansion mismatch between fibres and matrix, combined with the UV-induced reduction in stiffness.

8.4 UV and load

Although many studies have investigated the effects of UV on the mechanical properties of different types of FRPs [15], most experiments are limited to residual mechanical properties. UV radiation can accelerate the rate of photodegradation in materials, but it can also cause surface damage such as cracking, fading, and discolouration [130], with increased embrittlement [22, 132] and a reduction in material strength and stiffness [15]. UV radiation can induce cross-linking and chain scission [130] in the polymer matrix, altering its molecular structure and mechanical properties. When UV radiations are coupled with mechanical loads, the latter can promote crack propagation and chain scission, which yields shorter polymer segments with reduced load-carrying capacity, resulting in a decline in tensile strength [130] and leading to a reduction in stiffness [133].

8.5 Water/high moisture and elevated temperatures

In the investigation of material behaviour in moist or wet conditions, distilled or deionised water is generally used to maintain controlled testing parameters, with testing frequently conducted through immersion at elevated temperatures [29, 134]. The combination of water uptake and elevated temperatures is known as hydrothermal ageing. Various examples of hydrothermal ageing on CFRP and GFRP samples can be found in literature [135, 136].

As the individual effects of water and elevated temperatures on FRPs have been extensively discussed in previous sections, they will not be repeated. Irreversible plasticization of the bulk polymer in hot and moist conditions can induce interfacial debonding, exposing the reinforcing fibres [137]. Leaching, a process where soluble components are removed from the matrix by water or aqueous solutions, may also occur. This leads to the loss of important additives, plasticisers, and other functional components from the polymer, as well as altering the material's composition and properties [138]. S. Grammatikos et al. [139] investigated the effects of hot/wet aging on GFRPs with a PE resin for a duration of 222 days, through electrical property measurements at 60 °C, revealing that dissolution initiated within the first days of hot/wet aging and resulted in significant mass losses of 3.7% and 5.3% at temperatures of 60 °C and 80 °C, respectively.

A study conducted by Liu et al. [69], examined the absorption characteristics of CFRP rods under thermal conditions of 40, 60, and 80 °C, illustrated in Fig. 7. The Fickian diffusion model accurately represented the experimental data, indicating that higher temperatures led to an increased diffusion rate of water molecules in the radial direction of the CFRP rod. Additionally, high soaking temperatures demonstrated a rise in the total content of free water and bound water, with free water content of 0.52% at 80 °C compared to only 0.31% at 40 °C.

Heshmati M et al. [140] explored the effects of environmental ageing on GFRP and CFRP by evaluating 192 specimens exposed to five distinct ageing conditions. Samples

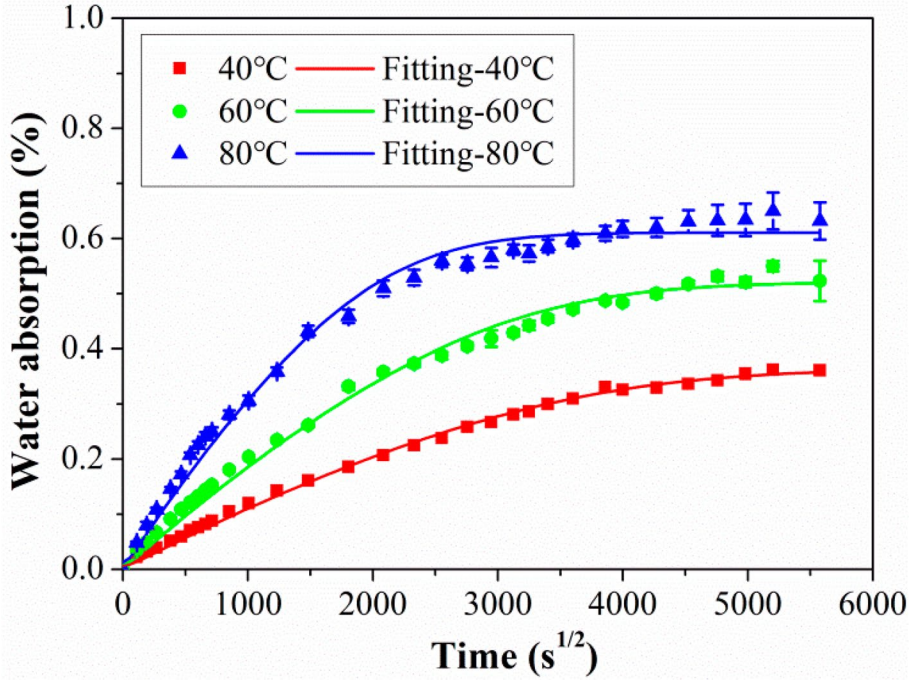


Fig. 7 CFRP rod at 40 °C, 60 °C, and 80 °C and corresponding water absorption curves [69]

were exposed to distilled (DW) and salt water (SW) at two temperatures (45˚C and 20˚C) and compared with exposure at 45˚C with 95% relative humidity (45RH). Focusing on the moisture ingress in distilled and saltwater at 20 °C and 45 °C into the CFRP material, 840 days led to an approximately 49 ± 7% and 41 ± 7% reduction in tensile strength, respectively. Although GFRP material experienced equivalent degradation in both conditions, CFRP showed sensitivity to extended exposure in saltwater. For the same immersion duration, saltwater immersion was found to be more harmful to the ILSS of CFRP than distilled water.

The phenomenon of immersion and adsorption exhibits distinct characteristics at room temperature in contrast to elevated temperatures. Elevated temperatures seem to facilitate a more rapid water absorption phenomenon within the CFRP specimens. The increased molecular mobility amplifies the likelihood of water molecules infiltrating the polymer matrix [69]. Concurrently, with rising temperatures, the matrix becomes more susceptible to softening and the functional groups within it more prone to hydrolysis. An increase in the number of voids and imperfections significantly amplifies the rate at which water molecules infiltrate the matrix. In contrast, at room temperature (25 °C), water molecules primarily infiltrate the composite through physical processes such as diffusion, leading to a comparatively lower rate of water absorption and molecular integration. For elevated temperatures at the moisture equilibrium point, the mass gain percentage at 70 °C was approximately 9.25 times greater than the corresponding value at RT [136].

8.6 Water/moisture and load

The combined effect of moisture exposure and mechanical loading results in significant interactions that affect the performance of composite materials. Moisture absorbed by the composite can act as a plasticiser, reducing the stiffness and strength of the matrix.

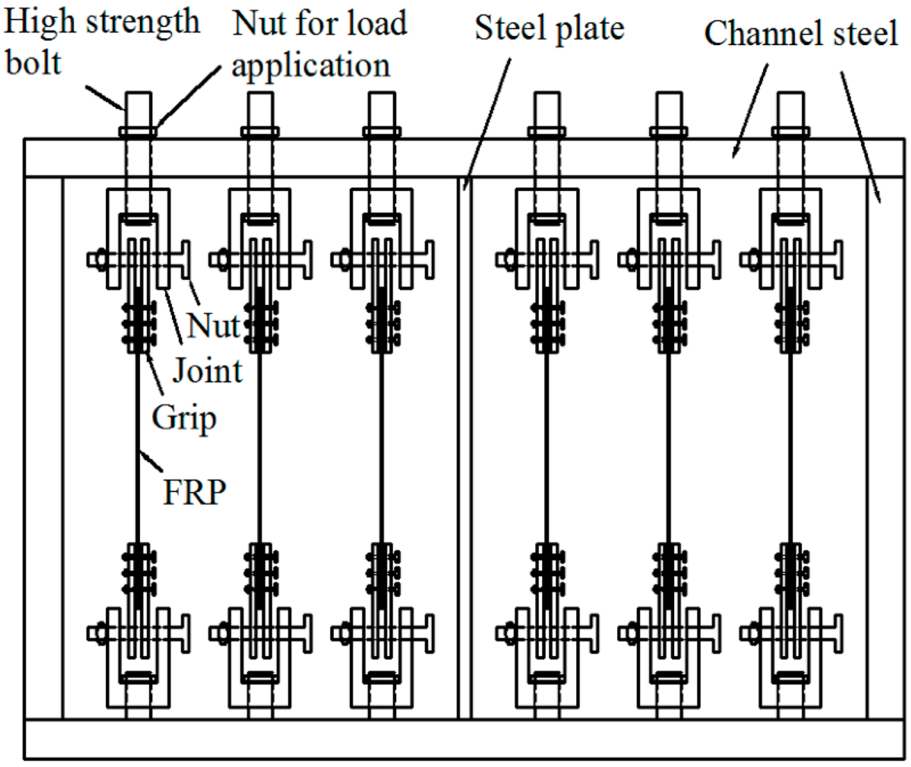


Fig. 8 A Bespoke sustained loading apparatus with a strain tracking clamp [11]

This, in turn, increases the susceptibility of the composite to mechanical damage and promotes the propagation of delamination under applied loads. If the liquid absorbed has specific solvents or aggressive chemicals such as acids and alkalis, it promotes environmental stress cracking (ESC). This occurs when the corrosive environment makes the composite more prone to cracking under applied stress [141]. The durability of pultruded CFRP plates under sustained bending strains (0%, 30%, or 50%) in seawater and water at room temperature was investigated by Kafodya et al. [142] over a period of 20 weeks. During the 20-week testing duration, the fibre-controlled properties showed minimal effects. In contrast, the resin-controlled properties experienced a more noticeable decline, with ILSS falling from 94.33 MPa to 67.02 MPa when the specimens were immersed and subjected to 50% loading strain. The results indicated that as the level of sustained bending increased, both the moisture absorption capacity and the diffusion coefficient decreased. Under strain, the evolution of swelling stresses coupled with polymer chains aligning in the direction of the strain decreases the free volume fraction of the polymer matrix. The increase in water ingress into the composite caused relaxation of the stress and an increase in strain, accelerating the post-curing process of the matrix. This initial increase in strain reduces the moisture uptake over time.

8.7 Moisture, elevated temperature and load

In situ, the combination of moisture, high temperature, and mechanical load presents a potential for severe degradation. Li S [11]. studied the hygrothermal ageing of FRP subjected to an applied strain corresponding to 30% and 60% of the ultimate load. The specimens were subjected to either individual factors or a combination of sustained stress with wet–dry cycles, freeze–thaw cycles and hygrothermal ageing, using a

bespoke fixture (Fig. 8). The sustained stress in the rig was limited to prevent creep rupture, following the recommendations set forth in ACI 440.2R-08 [143]. Since FRP materials experience creep or relaxation a reduction in the applied load of 1% and 3% was observed. Adjustment to the applied load was made with a bespoke arched strain clamp.

Without the application of load, the most significant degradation in tensile strength occurred during wet–dry exposure. The highest reduction in material performance was observed due to cyclic moisture absorption and desorption, with the CFRP specimens showing a decrease of about 7.5%, compared to the GFRP specimens, which exhibited a more pronounced reduction of 18.0% after 360 wet–dry cycles. In the absence of applied load, freeze–thaw exposure resulted in the least degradation, causing a reduction of 3.3% in the tensile strength of CFRP specimens, while GFRP specimens experienced a more significant reduction of 16.0%. In terms of loading coupled with freeze-thaw, CFRP again showed a negligible effect around 6.6% although GFRP had a 22.8% reduction. The author noted that GFRP exhibited greater vulnerability to both freeze–thaw cycles and sustained loading, which was primarily due to etching reactions within the material and the subsequent dissolution of the glass fibres.

However, any combination of environmental conditions and sustained loads had an almost negligible impact on the tensile modulus of both CFRP and GFRP specimens. Hygrothermal ageing in situ, on the other hand, demonstrated a more pronounced effect on the tensile strength of both CFRP and GFRP specimens, with a continuous decline in strength that accelerated at higher loading levels. Conditioning the material at 0%, 30% and 60% load levels, CFRP showed reductions of 6.3%, 10.6%, and 15.7%, respectively, and GFRP showed reductions of 16.6% and 27.9% in 0 and 30% loading cases, respectively. The author attributes this to the increase in tensile stress-induced microcracks that can promote water ingress and accelerate the damage mechanisms. Similar results by Ansari et al. [112], showed the initiation of micro-cracks during fatigue loading accelerated in the presence of moisture, leading to a more rapid degradation of the material. Whilst Meng et al. [144] on hygrothermal stress effects revealed that moisture can significantly alter the failure mechanisms of CFRP composites, leading to a higher likelihood of catastrophic failure under cyclic loading conditions.

Bin Hong et al. [145] conducted a comparative analysis of pultruded CFRP plates reinforced with either polyurethane (PU) or epoxy resin. The research analysed the effects of both water and seawater ingress under sustained bending stresses. Both systems, during the initial immersion stage, exhibited similar moisture absorption trends regardless of the applied bending strain, indicating no notable acceleration or inhibition of moisture uptake due to bending stress at this stage. This suggests that the matrix remains largely intact structurally, particularly in the surface region, and that the diffusion pathway is not yet significantly altered by strain-induced micro-damage. However, at later stages, notable reductions in performance were observed. At elevated temperatures, CFRP samples showed a significant recovery in their ILSS, particularly for water immersion. For water immersion studies at 20 °C and 60 °C, PU-based CFRP samples recovered the residual IPSS from initial degradations of 73.6% and 79.7–92.8% and 100.4%, respectively. In contrast, samples immersed in seawater exhibited lower recovery rates, with the residual ILSS of PU-based CFRPs improving to 88.8% and 95.2% from initial values of 71.9% and 69.6% at 20 °C and 60 °C, respectively. For water ingression at 60 °C, PU-based plates exhibited a higher initial IPSS than their control, which could be due

to post-curing. The reversible degradation in unstrained CFRP samples was primarily attributed to plasticization effects caused by moisture absorption. The irreversible degradation was linked to micro-crack formation due to swelling stresses. For CFRPs under bending strain, degradation mechanisms, including matrix shedding and the development of micro-cracks near boundaries in resin-rich areas, have been shown to result in diminished IPSS. PU-based CFRPs had narrower resin-deficient regions compared to their epoxy counterparts when exposed to seawater under high bending strain conditions, indicating a better interfacial bond.

9 Future requirements

Characterisation of pultruded composites under fatigue, temperature, and UV, typically uses a matrix-centric perspective due to the inherent resistance of carbon fibres to high temperatures and mechanical loading and the tendency for the matrix to govern the dominant failure mechanisms. The integration of additives such as carbon-based nanofillers represents one of the most promising pathways for addressing current limitations in thermal degradation, chemical degradation and interface failure.

Future work should assess the applicability of specific additives to pultrusion manufacturing and optimise nanofiller dispersion and alignment within the fibre or matrix phase to enhance load transfer efficiency, fatigue resistance, and temperature stability [58, 146].

Another avenue of research could focus on developing in situ testing methods that allow continuous tracking of degradation mechanisms and damage metrics through direct measurements of key mechanical and environmental parameters such as strain and stiffness evolution, temperature, and real-time moisture absorption rates. The integration of embedded sensors, such as optical fibre sensors [147] or piezoelectric materials embedded in carbon fibres [148] offers significant potential for advanced real-time structural health monitoring.

Although the pultrusion process frequently yields shaped geometries, testing is still commonly performed using coupon-based methods. This limits the interpretation of data, as such tests often fail to capture the true anisotropic stress distributions, geometric discontinuities, and manufacturing-induced defects present in actual structural profiles.

Future work must develop scalable, application-representative testing protocols that can be tailored to account for variability in CFRP, including differences in resin systems, fibre volume fractions, and fibre architectures. Moreover, methodologies should be developed to integrate environmental exposure with both static and dynamic mechanical loading, to replicate real-world conditions where environmental ageing and mechanical degradation occur concurrently. This also requires the advancement of combined environmental-fatigue testing chambers, capable of subjecting specimens to simultaneous loading and desired degradation mechanisms.

10 Conclusion

While limited research is available regarding the sequential or combined effects of environmental and mechanical stressors, current findings on the influence of UV, moisture, elevated temperatures, acidic/alkaline exposure, and fatigue, along with their potential synergistic interactions, have been highlighted. Among these, common and well-established interactions have been discussed, such as the effects of elevated temperatures,

which accelerate moisture ingress by increasing the kinetic energy of the water molecules, thereby enhancing the potential for diffusion. UV-induced surface degradation through photo-oxidative reactions, causing embrittlement and cracking, which facilitates additional pathways for absorption. However, as the number of mechanisms begins to increase, comprehension begins to waver, and findings begin to diversify. While some UV-moisture studies report significant reductions in mechanical properties (29% reduction in transverse tensile strength) and significant surface deterioration from early-stage exposure, other literature observes only superficial surface effects with negligible impact on properties. This indicates that synergies are highly dependent on resin type, fibre architecture, and the nature of the environmental exposure or load applied.

In addition, synergistic interactions among multiple degradation mechanisms, such as surface particle erosion or combined environmental exposure with static and dynamic loads, influence microstructural evolution and failure modes. This remains an area of active research and is not yet fully characterised. Lastly, the limited available data are derived from accelerated ageing protocols and small-scale testing, which may not fully represent complex or shaped geometries, nor real-world service conditions. Therefore, this review has correlated current data, discussed experimental variations in existing protocols, and highlighted both the advantages and limitations of current testing procedures. These insights should inform the development of more rigorous methods to support comprehensive and realistic design, modelling, and long-term reliability assessments of pultruded FRP structures in applications such as civil infrastructure and marine environments.

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Author contributions
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Data availability
No datasets were generated or analysed during the current study.

Declarations

Ethics and consent to participate
Not applicable.

Consent for publication
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