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Review

Hygrothermal ageing of composite structures. Part 1: Technical review

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ABSTRACT

The aim of this work is to review the literature of hygrothermal ageing in composite structures, focusing on the effects of moisture absorption on mechanical properties, damage behavior and degradation mechanisms responsible for changes in performance. Potential causes that can lead to failures are detected and the main variables that influence the ageing are taken into account: these include the surrounding environment and climate conditions, which appear to be determinant. Secondly, a case study analysis on previous accidents involving aircraft composite structures damaged by moisture is presented. This reveals that some components, such as sandwich panels and adhesive-bonded-joints, are particularly affected by hygrothermal ageing, and thus require a detailed assessment in terms of humidity deterioration. Further insights on the main industrial applications of these components, such as wind and tidal turbine, are showcased and crucial issues are highlighted. Moreover bio-composites behaviour in harsh environments are analyzed, showing drawbacks and advantages.

1. Introduction to moisture related issue in composite structural components

During last decades the use of composite materials has remarkably increased, especially in the aerospace industry, due to higher mechanical property (strength, stiffness and fatigue resistance above all) compared to traditional metallic materials, but also due to other advantages such as higher strength-to-weight ratio, corrosion and impact resistance, design and production process flexibility, low thermal expansion coefficient and high temperature resistance as described by E. Kececi in [1], Y.F. Niu et al. in [2], N. Zimmermann and P.H. Wang in [3], B. C. Ray et al. in [4] and A. Krauklis in [5]. Composite materials are widely used in the aerospace sector for primary structures such as fuselage, wing, flaps, fairings, but also for other non-structural interior aircraft parts. Another common application of these advanced materials is for wind and tidal turbine blades. Above all, the main reason of the adoption of composites in aerospace field consist in their light weight compared to traditional configurations, considering the fact that weight is the main parameter taken into account during the design process of an aircraft, since it contributes to consume less fuel, leading to economic savings for airline companies as stated by C. Kassapoglou in [6]. Moreover, it must be taken in account, that the attention to emissions reduction is also one of the main concerns for the actual aircraft market, with an increasing interest among airlines about sustainability and green fuel trends.

Composite structures used for aircrafts, wind and tidal turbine blades are placed in direct contact with the external environment (humid air of the atmosphere or sea water), so they easily interact with atmospheric agents or water and are more prone to undergo humidity damages during their operations. In fact, composite materials absorb more moisture from the environment, compared to traditional materials, with a detrimental effect on mechanical, physical, electrical, thermal properties and service life reduction as shown by K. Shetty et al. in [7] and B. C. Ray et al. in [4]. More in detail, E. Kececi and R. Asmatulo in [8], observed that some advanced composite structural components, like sandwich panels and adhesive bonded joints (evolution of the simple composite laminate), have a conformation, from the morphological and design point of view, that tends to enhance the moisture ingress, since they are not perfectly isolated from the external environment and are realized by connecting more parts together (laminate layers, substrates, adhesives, honeycomb core), with higher risk of water penetration at the interfaces.

In the aviation field, since the damages induced by moisture absorption can strongly impact the aircraft performance, the reliability standards must be kept high in order to satisfy the requirements imposed by the aviation regulations. D. A. Katsaprakakis et al. in [9] underline that high safety levels are required also for wind and tidal turbine blades, which are particularly expensive. For this reason, effective solutions to the humidity issue and hygrothermal ageing must be adopted in order to guarantee safe operations and extend the operational life of

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composite structural components.

The part 1 of the review is divided in two main chapter. An historical review is presented in Chapter 2, analyzing accidents from the early 1990 s (1989 Concorde) to the present (2015 Airbus A310) occurred due to moisture uptake. From this chapter is possible to points out all kinds of structures that are particularly affected by hygrothermal ageing. Chapter 3 analyzed structural components identified in the previews chapter particularly subjected to humidity degradation and structures that experiment a very harsh environment, such as wind turbine blades and tidal turbines. Moreover, a subsection is dedicated to bio-composite materials, that are showing a growing use thanks their ecosustainability but present several issues when operating in humid environment.

2. Case study analysis: History of accidents caused by moisture uptake

Different approaches can be considered to deal with the problem of humidity/associated damages in composite structures. Among these, an historical perspective can be useful in the first phase of the study, especially to find out which are the most affected composite structural components by humidity deterioration, through a detailed research of the failed components originated by moisture absorption, given by the investigation of previous accidents happened in the last decades. In the aviation history there are several cases of failures involving aircraft composite parts, especially in the design form of honeycomb sandwich panels and adhesive bonded joints. The most recurring event was the separation of portions of the control surfaces, lost during the flight; however, the amount of damage was not so substantial to impede a safe landing for the aircraft.

2.1. Concorde

One of the most exemplar case study is that of the Concorde, with at least six rudder failures (in-flight separation of some portions, as can be seen in Fig. 1) during its operations over 14 years, from 1989 to 2003 [3]. The rudder used for the Concorde was produced as a honeycomb sandwich structure, formed by adhering two rigid thin sheets of composite with a low-density honeycomb core, which is made by empty cells to minimize the weight, but at the same time inducing the trapping of moisture inside them.

Investigation followed the accident and revealed that the rudder separation was determined by the presence of delamination of the honeycomb core and skin (composite layers detachment). Moreover, the adhesive bond strength was deteriorated and the surface between the honeycomb adhesive and skin was damaged by corrosion, both as a consequence of moisture penetration into the structure, with, in some cases, subsequent ice formation, which enhanced the deterioration of the structure [3]. Another possible cause and co-factor of the failure was the presence of pre-existent and un-repaired defects or micro-cracks not seen during previous maintenance check [3]. In addition, the installation of rivets after bond curing of the structure may have promoted cracks and adhesive strength reduction, leading to debonding and



Fig. 1. Rudder failure, G-BOAF, 1989. Adapted from [10].

rudder failure [3]. N. Zimmermann and P. H. Wang in [3] and the Australia's national transport safety investigator in [11] concluded that the failure was mainly attributed to hygrothermal ageing and the combined effect of moisture presence and strong thermal cycles was considered determinant. The investigation process, driven also by visual inspections, exhibited the main reasons of these failures, mainly linked to adhesive bond strength deterioration and corrosion of the interface surface between the core and the skin, promoted and enhanced by the penetration of moisture inside the structure. Two of the air frames involved in the accidents deployed a rudder with the same serial number, meaning that the two components were manufactured as a pair. Since both failed in similar ways, the investigation focused on the production phase and maintenance techniques. The results showed that the rudder failure was caused by the separation between the rudder skin and the adhesive, in turn induced by water penetration followed by ice formation. Deeper studies revealed that the degradation of the structure was enhanced by using a wrong repair procedure which exploited the paint stripper tool, responsible of the humidity damage onset and amplification, generating cracks and softening of the adhesive [3].

One more cause of failure of the honeycomb due to moisture ingestion analyzed by investigations following accidents is the skin-to-core separation, verified also by realizing different kinds of tests on the failed rudders, whose results showed that the moisture penetration inside the bondline was caused by inadequate bonding between the skin and the core. D. B. Miracle et al. in [12] underline that in many cases, the presence of river patterns on the epoxy resin that remained attached to the adhesive allowed to detect the direction of skin separation and the origin of the failure.

From the Concorde series of accidents, involving the aircraft rudder composite sandwich skin-to-core separation, the general conclusion obtained from the investigations was that the rudder failure occurred as a consequence of the inadequate bonding between the skin and the core, possibly due to moisture introduction into the bondline [3].

2.2. f18

Structural failure of composite honeycomb sandwich rudder due to moisture ingress occurred also in many exemplars of F-18 military aircraft, specifically in-flight disintegration of the rudder. Water retention in honeycomb cells and skin-to-core bondline degradation were found during investigations performed by J.S. Giguere in [13]. Investigation process aimed at detecting direct water penetration paths, which were enhanced in areas of the rudder near leading edge hinges, grounding studs and a jig holes, all elements that acted as water ingress points as showed by C. Li et al. in [14].

2.3. Boeing 767

Another interesting case was the inspection of part Boeing 767 fleet from United Airlines during maintenance, in order to detect water absorption in sandwich structures and its amount. The most critical component was found by J.E. Shafizadeh et al. in [15] to be the nose landing gear doors (vain undercarriage) made of composite honeycomb structure, with a large amount of liquid water accumulation (about 20 kg), being the cells fully filled.

Main reasons of deterioration were detected, such as: skin porosity, internal voids, micro-cracks or delaminations due to pre-existing damages (impact, production or maintenance), degraded fillers used to reduce micro-voids. Also freeze-thaw cycles, happening if the system changes altitude in a recurrent way, put a strain on the material: when water is accumulating inside the composite, a reduction of temperature (at high altitudes, up to -40°C inside the core at 9000 m) makes it freeze, the again it melts when the aircraft lands. If these expansion/contraction cycles are repeated for a long period of time, stresses are generated near cavities in which water is present and on the honeycomb core walls so that delaminations and debondings can occur [15]. In more

detail, after moisture ingress in the composite thanks to surface imperfections inherent to the material morphology, these cycles lead to micro-cracks formation in the bulk region of the laminate sheets and amplify the voids, which start to link together generating paths that enable a further penetration of water in depth. This propagation of voids moves from the external surface towards the honeycomb cells, which are progressively filled by water [15]. Then, another mechanism of degradation on the sandwich structure induced by these thermal cycles is the separation of the external skin from the core, due to an increase of the trapped water pressure acting on both sides, caused by an increase of temperature, as observed by G. Kim et al. in [16]. Additional critical issues in the front landing gear compartment doors are linked to the need to make holes in the honeycomb to connect the door structure to the fuselage and the actuators necessary for the gear handling. Holes are drilled and filled with special thermosetting and insulating material to strengthen connections and avoid water penetration, but this filler material deteriorates over time, due to thermal and mechanical cycles, so it facilitates the formation of defects and voids and allows the passage of water through preferential paths, towards the core of the panel. Sandwich panel thickness strongly influences the water absorption rate and build-up, thus the damage intensity. This fact also explain why vain undercarriage for the front gears was the most critical component, as seen from investigation results of the Boeing 767. In fact, the honeycomb core of these sandwich panels is very thin (around 0.025 m) compared to other composite parts [15].

2.4. Airbus A330-2000s, A340-200s, A340-300s

Moisture ingress issues involved also several Airbus A330-200s, A340-200s and A340-300s, which registered structural degradation linked to moisture ingress during their operations in the last decades: disbonded areas found inside the elevator and stabilizer sandwich panels led to an airworthiness directive from FAA imposing additional inspections and maintenance on that components to avoid water ingress as reported by N. Ischdonat in [17,14].

One of the most recent accidents linked to humidity absorption is dated 8 May 2015, when a Royal Canadian Air Force (RCAF) Airbus A310 (known as a CC-150 Polaris) reported an in-flight loss of part of an elevator [18]. After a safe landing, visual inspections were performed, showing debonding and loss of a part of the right elevator trailing edge, Fig. 2. The combination of high surface temperature, promoted by the dark paint scheme of the component, and moisture absorption, was considered responsible of the failure, affecting the properties of the structural adhesive located between the elevator skin and honeycomb core. The horizontal stabilizer was further analyzed, detecting an irregularity in the paint, not duplicated on the opposite elevator, and a delaminated length from 0.3 m to 1,5 m along stabilizer span [18]. The accident pushed the engineers to establish several preventive actions on the entire CC150 Polaris fleet, including the repaint of composite parts



Fig. 2. View of damaged right elevator trailing edge of an A310 Polaris. Adapted from [18].

in light-colour to avoid excessive heating, the correction of the preventive maintenance program, by increasing the inspection frequency of the composite structures, the addition of X-ray analysis technique as a standard procedure and the monitoring of the state of the sealant during every inspection. Furthermore, an investigation on the effects of dark paints on the present-day RCAF fleet is in progress, in order to avoid new failures of the same type [18].

From what concerns the safety aspect, the investigations of the aforementioned accidents showed that the failures strictly associated to humidity issues were not critical, since they did not compromise the main functionality of the aircrafts, which were able to land safely. All these reported cases were not as severe to cause a catastrophic failure of the aircraft, with damages assessed as minor, but the evidence highlighted by investigation process was that they were, for the most part, recurring in very similar ways in different aircrafts of the same type, meaning that the procedures applied during the manufacturing process or maintenance were not adequate. In many cases, the problem was underestimated by the technical division of airline companies, leading to replicate the same failures.

Some investigations done by big airline companies like British Airways demonstrate explicitly how relevant is the impact of humidity damages on composite aircraft structures from the economical point of view. A study by M. J. Morris of British Airways [19] was realized in order to estimate the cost linked to the maintenance actions required to counteract humidity damages. In detail, twelve spoiler panels were repaired and for each one an average weight increment of 1,5 kg was measured, for a total cost of 150,000 £ for every year [19]. Considering the fact that many other composite components undergo moisture degradation, the overall effort for the maintenance of an entire fleet is relevant for an airline company, from the economic point of view.

2.5. Remarks

The tendency of composite materials to suffer damage when working in harsh environments makes clear that the humidity issue for composites must not be underestimated and need instead rigorous and deep study, in order to evaluate the impact on the system performance and assess the reduction of the operative life. A further demonstration of this statement was given by the analysis of previous accidents involving composite structures which suffered from moisture absorption during their operations. The high frequency of occurrences is a proof of possible negative implications of the hygrothermal ageing in composites, especially from the safety point of view, which is a priority in industrial fields like aviation. In some cases the damages were substantial, but without compromising the basic functionality of the aircraft, so the pilots were able to perform a safe emergency landing followed by investigations which lead to the identification of the main damaged areas and the causes of the failures. However, the proposed overview shows how critical can be the humidity problem for composites: the frequency of the accidents and issues related to moisture uptake into composite aircraft structures during the last decades is quite high and is an evidence that this problem cannot be neglected nor underestimated, but on the contrary it needs a great attention in order to face every possible detrimental consequence and keep high the performance of the system, avoiding down-times for repairs or replacements with negative economic implications. Furthermore, as highlighted by the case study analysis, some failures occurred in recent years, like that of the Royal Canadian Air Force Airbus A310 Polaris, dated 2015. These occurrences witness the fact that damages induced in composite components by humidity are still an unsolved issue, leading to structural breakdown, urgent repair and replacements, with relevant economical losses and safety concerns. The case study analysis makes also clear that failures linked to moisture absorption can lead to critical issues especially if associated with wrong maintenance procedures and lack of real-time monitoring of the health status of the structural component. Thus, innovative and cost saving maintenance techniques are of the utmost

importance, as well as the design of composite structures (especially the choice of new resin and fiber reinforcement materials showing a better behaviour when put in a humid environment) together with the production process. Another main task is the possibility to monitor in real-time, during the course of a flight, the behaviour of every structural component, thus achieving a prediction to foresee a possible reduction in the performance, as a consequence of a damage induced by humidity. Such information can be obtained by using a structural health monitoring system (SHM), which can provide real-time data on the working conditions of the aircraft including moisture content. The SHM brings many advantages, above all the reduction of the failure rate, since with the most advanced systems every damage, even the smallest one, can be detected much earlier than the failure occurrence. C. Touloup et al. in [20] and P. Synaszko et al. in [21] state that emergency landings, which generally lead to the grounding of the aircraft with economical losses, can be avoided. Nonetheless, it is still crucial for the safety of the aviation industry to properly investigate and analyze failed structures, since the results of these studies can be used as the basis for future safety improvements. [3].

For these reasons, the research of innovative and effective solutions against hygrothermal ageing is essential to avoid future accidents and failures. Another observation comes from the analysis of previous accidents: the majority of the issues due to moisture absorption arose in aircraft composite components involving sandwich panels and adhesive bonded joints, which, by construction, are made of different parts connected together, thus increasing the propensity to absorb water and being damaged during operations. Therefore, a section is dedicated further on.

3. Main composite structural components subjected to humidity damages

As concluded from the analysis of the investigation of previous accidents involving composite structures which suffered hygrothermal ageing, the most relevant composite components in which the humidity effects could be substantial are sandwich panels and adhesives bonded joints, both widely used in aviation field and in other industrial applications, especially for wind and tidal turbine composite blades. Due to their less compact conformation (presence of empty spaces inside the core), with respect to the standard composite laminate design, and production process complexity, sandwich panels are one of the most critical composite structures to undergo humidity damages, together with adhesive bonded joints, so they need a detailed study and solutions to minimize hygrothermal ageing effects [8,16].

The problem of humidity for aircraft composite structures is often associated to the use of honeycomb-core sandwich panels, that are extensively deployed for several structural parts of an aircraft, including rudder, aileron, flap and spoiler thanks to the increased strength and stiffness given to the whole structure, excellent fatigue and corrosion resistance and also a weight reduction which is one of the most important parameters taken into account during the design of an aircraft structure, since it helps to reduce the fuel consumption with great advantages from an economic point of view [8,21].

The skin plies are the external layers and are made of matrix and reinforcement fibers (in general carbon or glass fibers/epoxy resin). Matrix or resin material primary goal is to transfer stresses between reinforcements, to keep fibers to get her and to protect them from environmental aggression and impacts. Reinforcement fibers provide high mechanical properties like strength and stiffness. Honeycomb core is the central region of the sandwich panel, the thickest one and with an high empty space fraction, to minimize the weight of the whole structure and improve the stiffness of thin composite laminates. Adhesives are composite materials used to link different materials by bonding, providing strong adhesion at the interface between the composite sheets and the honeycomb core [8,1,16]. Every component which forms the sandwich structure is subject to humidity absorption: the external

laminate sheets are the first to suffer moisture presence, which than progresses towards the adhesive layer and finally accumulates inside the honeycomb core.

3.1. Sandwich structures

Sandwich structures have a bad reputation because of several problems and accidents reported in the open literature. B. Castanié et al. in [22], F.C. Campbell in [23] and G. Kim and R. Sterkenburg in [24] stated that issues are mainly linked to closed honeycomb cells that trap moisture, resistance reduction of bonded joints between the skin and the core, or degradation of the poli-aramidic honeycomb during the freeze-thaw cycles that follow changes in external temperatures during flights. Moreover, M. Morris in [19] stated that a honeycomb structure can double its weight following moisture uptake, which gives an idea of the severity of the humidity problem in sandwich structures. Sandwich panels are widely used for external structural applications, so they are often in direct contact with the environment in which they are used, which means that they can easily be attacked by humidity.

D.M. Cise and R.S. Lakes in [25] noted that the matrix commonly used is an epoxy resin, which is very sensible to moisture since it is an hydrophilic material, so it has a natural tendency to absorb water molecules and hold back moisture on the surface and in the bulk region. This feature of epoxies can be adverse, because humidity absorption can cause, after long exposures (hygrothermal ageing) processes those bring to a reduction of both physical and chemical properties of the material: processes like hydrolysis, which is a chemical reaction between water molecules and polymer ones that induces a chain breakage, lead to irreversible damages.

Also the morphological structure of the host material enhances the humidity absorption: it contains many porosities and voids, regions in which humidity and water can accumulate in time. Moreover, moisture diffusion is promoted by the morphology of the honeycomb structure, which is less compact with respect to solid laminates and the filler is not perfectly isolated and sealed from the external environment [8,16]. In addition, in the case of sandwich structures, the core region is designed to be as light as possible, so empty honeycomb cores can be easily filled with water coming from the composite sheets through the interface [16]. If the moisture absorbed remains trapped inside the core, it leads to weight gain and irreversible damages to the structure as observed by A.E. Marble et al. in [26]. The internal void fraction is further increased if the curing process is not strict or if inappropriate maintenance techniques are applied, with poor sealing repair leading to the birth of new micro-cracks that make it easier for water to penetrate in depth. Added contributing causes of moisture diffusion are the core topology design and the presence of not detected impact damages during maintenance [22]. Temperature, relative humidity and exposure times are the most relevant parameters which influence the absorption rate as underlined by L.S. Sutherland in [27]. High temperatures increase the pressure inside the honeycomb cells causing detachment from the sheets [16].

In sandwich structures for aviation, thermal cycles (freeze-thaw cycles) happen when the aircraft changes altitude, stressing the material, leading to a reduction of fatigue life. When water is accumulating inside the composite, a reduction of temperature makes it freeze, the again it melts when the aircraft lands. In standard operations, an aircraft pass from $-50\text{ }^{\circ}\text{C}$ in cruise flight to over $30\text{ }^{\circ}\text{C}$ after landing, which means strong thermal solicitations. J.E. Shafizadeh et al. in [15], G. Kim et al. in [16] and P. Synaszki et al. in [21] showed that if these cycles are repeated for a long period of time, stresses are generated near cavities in which water is present and on the honeycomb core walls so that delaminations and debondings can occur, and new paths for diffusion are generated, further increasing the damage. F. Yin et al. in [28] found that water molecules are responsible of the destruction of hydrogen bonds which form the network of the poly-aramidic honeycomb, leading to a loss of mechanical properties. D. Larobina et al. in [29] showed that inadequate bonding between plies and honeycomb core is also

responsible of water penetration inside the material [3]. Lastly, combined effects of impact damages from collisions with small objects strongly affect humidity absorption [21,16]. In fact, when a composite laminate is hit, both the fibers and the resin are crushed in the impacted area; meanwhile, the stricken laminate triggers interlaminar shear failures leading to delaminations, which can generate new preferential paths for water ingress, as showed by M.R. Woodward and R. Stover in [30,22].

The first consequence of the absorption of water into composite structures is a physical one: as water molecules move through the resin, the polymeric matrix undergoes a plasticization phase, which can be defined as a change in the morphology of the component (dimensional change) [5]. A. Regazzi et al. in [31] and B.C.M. Rocha et al. in [32] stated that when water molecules are absorbed into the polymer, they induce a reorganization of its molecular chains, by interacting with polar groups and reducing the intermolecular bond forces, thus increasing the chain mobility, so that the material passes from a glassy (stiff and brittle) to a rubbery (softer and tough) state, the so-called plasticization. This process leads to a reduction, mostly temporary and reversible, of physical properties (glass transition temperature) and mechanical properties (like resistance modulus, strength and stiffness) and an increase of free volume inside the material (swelling), thus causing a rise in the absorption rate. Moreover, B.C. Ray and D. Rathore in [33] noted that an increase in the weight is also detected in the first phase of the hygrothermal ageing process due to water ingress. Then, for long ageing times, multiple secondary effects (yellowing, leaching, dissolution, hydrolysis, oxidation) occur not only in the resin but also involving fibers and the fiber/resin interface, with an additional change in weight and volume of the composite, which is in general not reversible. High stress areas can be found in the interface zone between honeycomb core and sheets of composite and between fibers and matrix, due to the differential swelling as showed by B.C. Ray in [34]. Corrosion and delaminations at interface can also be present [16]. A. Simar et al. [35] evince the presence of thermo-oxidation phenomena during hygrothermal ageing under ambient air at 70 °C and 90 °C of an epoxy/amine network. The coupling between humid and thermo-oxidation phenomena implies some chemical-physical changes in the polymer such as: polymer color changes, irreversible glass transition temperature decrease, resin embrittlement, occurrence of a property gradient from the edge to the sample center, anomalies respect to the Fick's diffusion law and small residual mass fraction in re-dried specimens. The same authors in [36] present a novel experimental/numerical method able to decouple water and oxygen diffusion phenomena and to prove the occurrence of thermo-oxidation during hygrothermal aging.

For longer ageing times, it is common to notice debonding and micro-cracks in the interface region between the skin and the core, induced by a degradation of the additives used to form the chemical adhesion needed to create a strong interface. The main humidity absorption consequences are the generation of patches of corrosion of the skin layer and the reduction of resistance of bonded joints which unite the skin and the core. The adhesives suffer deterioration and their tensile and bonding strength reduces [3]. A reduction of service life is frequently detected, as a consequence of damage induced by water uptake, so improved maintenance and enhanced inspection techniques must be applied to avoid these kind of failures.

J Mei et al. [37] conducted accelerated moisture diffusion tests on a carbon fiber-reinforced polymer (CFRP) composite in the form of a sandwich panel with innovative core structures (like strut-based lattices, realized by additive manufacturing) to investigate the moisture absorption behaviour and hygrothermal ageing effects on the mechanical properties. Temperature had a significant influence on the moisture absorption behavior. The equilibrium moisture content and diffusion coefficient increased as temperature increased, following the Arrhenius equation. They obtained the total moisture content in the sandwich panel during immersion tests; the relation between the moisture content M_t and the square root of the specimen immersion time \sqrt{t} is shown in

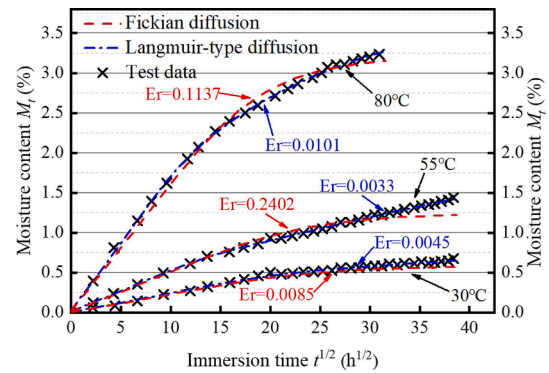


Fig. 3. Diffusion curves: numerical and experimental data of moisture content at 30 °C, 55 °C and 80 °C. Adapted from [37].

Fig. 3, which compares the experimental results with the outcomes from two diffusion models (Fick's and Langmuir-type).

In the initial part of the curves of moisture diffusion, the moisture content increases linearly, and then gradually slows down until a plateau is reached, which is the saturation condition, at the maximum moisture content. Since the temperature influences the diffusivity, it has also an effect on the time to reach the saturation condition. High temperature levels mean high diffusion and so a reduced saturation time. The compressive properties were also tested after hygrothermal ageing, through uniaxial compression tests in the direction of the thickness of the panel, after exposure to different temperature and humidity. The experimental results indicated that the compressive modulus $E_{(t,T)}$ and strength $\sigma_{(t,T)}$ of each composite strut and that of the whole sandwich panel reduced due to the combined effect of temperature and humidity absorption: prolonged ageing time and higher temperature resulted in a sensible drop of mechanical properties [37].

3.2. Adhesive joints

The adhesive bonded joints are widely used in many key industrial sectors, allowing the construction of lightweight and multi-material structures, combining polymers, composites and metals. Like for other composite structures, also composite adhesives are applied in the aerospace sector (especially for wing skins and control surfaces) to improve mechanical properties and reduce the structural weight. Their application to structural components made of fiberreinforced composites has increased significantly in recent years. However, C.S.P. Borges et al. in [38], G. Viana et al. in [39], S. Sugiman et al. in [40], Y. Hua et al. in [41], X. Han et al. in [42], C. V. Katsiropoulos et al. in [43] and H.R. Gualberto et al. in [44] underlined that adhesives are generally polymeric materials, which suffer from environmental conditions, such as moisture and water absorption, possibly leading to operative life reduction and failures. Moreover, M.D. Banea and L.F.M. da Silva in [45] stated that prolonged exposure or even short-term exposure to elevated temperatures will often produce irreversible chemical and physical changes within adhesives. As the temperature increases, the bond strength decreases.

H.R. Gualberto et al in [44] defined the adhesive bonding as a material joining process in which an adhesive (in composite), placed between the adherent surfaces (in composite or metal), solidifies to produce an adhesive bond. The main goals of composite adhesives are: link together composite/metal panels; connect external composite layers with the honeycomb core in sandwich panels; repair cracks. Adhesively bonded joints are increasing alternatives to mechanical joining methods in engineering applications, since they provide many advantages over traditional mechanical fasteners like bolts or welding. The use of bonding methods with adhesives is convenient to limit the stress concentration which arise inevitably when a hole is drilled into the material and achieve a better load distribution (more uniform

distribution of stresses) and fatigue resistance [44]. Moreover, M.D. Banea and L.F.M. da Silva in [45] stated that traditional fasteners can generate fibers cutting, leading to stress concentrations reducing the structural integrity. E.

Moutsompegka et al. in [46] underlined the main disadvantage of adhesives: the degree of uncertainty in the long-term usage, since the prolonged exposition to harsh humid environments can lead to a major loss of performance [44].

M. Heshmati et al. in [47] studied adhesive bonded joints with both adhesive and adherend made of composite material, they found that the water permeation into the material can occur in three different ways: diffusion in the adhesive layer; diffusion through the interface between the adhesive and the adherends; absorption by the pores of the adherend. Ageing process has been studied by R. Léger et al. in [48], they found that it leads to micro-cracks formation and loss of mechanical properties, with a reduction of the joint strength, caused by the softening of the adhesive after plasticization and by stresses induced by swelling in the adhesive and at the interface. Y. Bai et al. in [49] presented another issue occurred when adhesive and adherend materials are different. Since they have different expansion coefficient, this leads to differential swelling and so intense stress levels at the interface, which is the most critical region of the adhesive, where the moisture accumulates more quickly with consequent damage formation. Differential swelling at the interface between the adhesive and the adherent can lead to the formation of micro-cracks and new preferential paths for diffusion, intensifying the moisture absorption and consequently increasing the degradation. Different failure modes caused by hygrothermal ageing are possible for the adhesives: cohesive, adhesive and substrate failure (Fig. 4).

During the ageing process, observations showed that the failure mode switches from cohesive to adhesive, which is more critical for the structural integrity of the adhesive, since in that conditions the interface is very weak and is responsible of the failure. The ideal performance of the adhesive joint should lead to cohesive failure: the interface does not fail before the adhesive failure itself [43]. G.M.S.O. Viana et al in [51], J. M. Sousa et al in [52] and G. Zheng et al. in [53] studied, respectively,

the influence of temperature, relative humidity and exposure time in the diffusion of moisture in adhesives. High temperature levels are also responsible of a faster transition from cohesive to adhesive failure mode as highlighted by S. Budhe et al. in [54,55], A. Mubashar et al. in [56] and R.A. Gledhill and A.J. Kinloch in [57].

From what concerns the moisture effect on interfacial properties of adhesive joints, C.S.P. Borge et al. [38] analyzed how detrimental can be the trapping of humidity at the bonded joint interface, considered the most critical region of the component to suffer ageing damages. Although moisture degrade the adhesive, the failure of a bonded joint is often ultimately interfacial. As previously pointed out, adhesive bonded joints are particularly sensitive to moisture absorption, since it can occur following various paths inside pre-existing micro-cracks, pores and additional entrances (through the adhesive, through the substrate and at the interface between the adhesive and the substrate). Moreover, several studies conducted by J. Comyn in [58], B.C. Duncan and W.R. Broughton in [59], M.P. Zanni-Deffarges and M.E.R. Shanahan in [60] and S. Budhe et al. in [61] underlined the importance, in the diffusion process in adhesives, of capillarity effects, which strongly enhance the diffusion rate along the adhesive/adherend interface, with the risk of causing premature bonding failures [38,43]. This also explains why tests results show a higher diffusion coefficient through the joint interface with respect to the one in the bulk adhesive [38,43,59,60].

Water can both accumulate at the interface region or being absorbed by the bulk adhesive and the substrate, with higher risk of hydrolysis for prolonged ageing times, thus affecting the performance of the joints. If the moisture is absorbed by the bulk adhesive, plasticization and swelling occur since it has a hydrophilic behaviour and their mechanical properties decrease. This first effect of hygrothermal ageing is in general recoverable, while if water penetrates at the adhesive/substrate or fiber/resin interface, it can disrupt interfacial bonds (hydrolysis, cracks, debonding) leading to non-reversible reduction of strength, fracture toughness and loss of structural integrity. A. Mubashar et al. in [62] and in other different studies [42,43,55] showed that only the part associated to adhesive plasticization can be recovered, not the resting contribution of the interface.

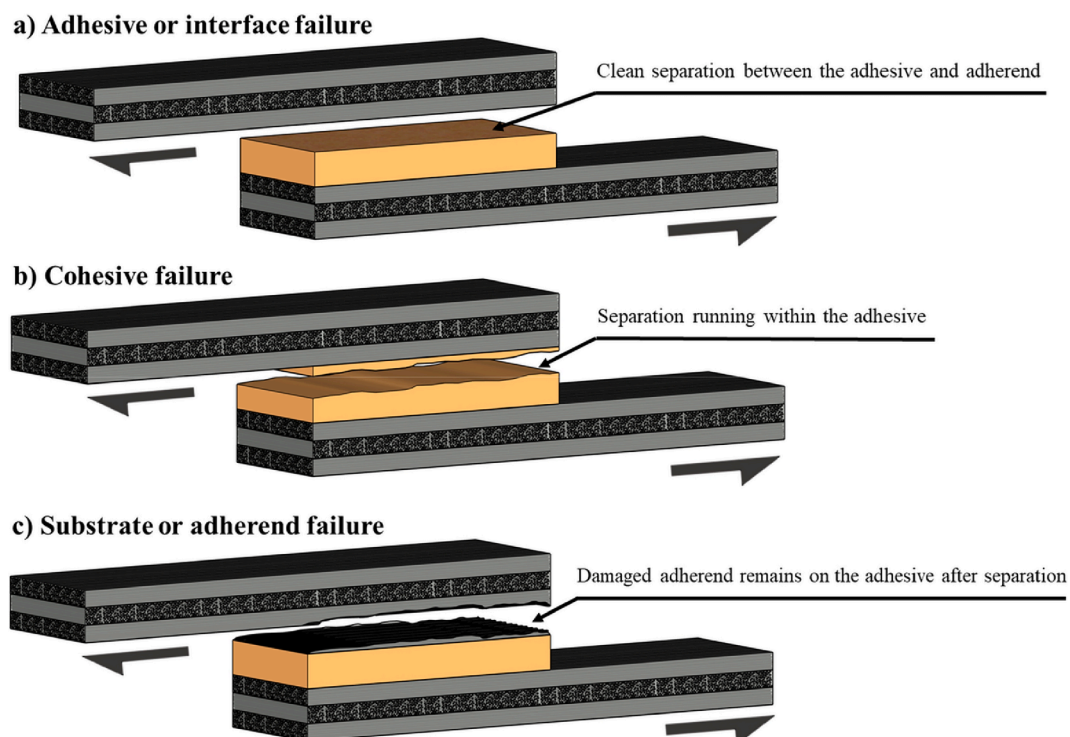


Fig. 4. Adhesive (a), cohesive (b) and substrate failure (c). Adapted from [50].

With respect to the standard composite laminates, the ones that use adhesives are made of different parts joined together, so water diffusion is promoted at the interfaces and occurs faster because of several diffusion paths, possibly leading to a failure within adhesive and substrate [38]. Without environmental attack, failure occurs the adhesive layer (cohesive failure). In this case, the interface between the adhesive and the substrate is not degraded by moisture uptake, so it keeps high mechanical properties without failing. However, if moisture is absorbed by adhesive, the interface becomes weaker over time and is responsible of the failure: in this case, an adhesive failure occurs, since the damage shifts from the bulk adhesive towards the interface region.

F. Cavodeau et al. in [63] identify the diffusion through the adhesive/substrate interface as the key element for adhesive bonded joints damage due to moisture uptake, possibly leading to a complete interface debonding. A.J.

Kinloch et al. in [64] stated that the interface is the most favorable place for crack propagation, promoted by micro-voids which enhance moisture build-up [48]. The main conclusion is that the diffusion through the interface is responsible of the majority of damages in the adhesive joints, with reduction of joint strength and higher likelihood of interfacial failure.

Not only adhesive and the interface also composite substrate can absorb moisture and transport water molecules toward the interface, leading to further deterioration, while in case of metallic substrates the higher risk is associated to the corrosion with presence of iron oxides and possible modification of bonding chemical structure as well as change of adhesive composition close to interface, leading to performance losses. In addition, a metallic substrate is not subjected to volume expansion during ageing, differently from the composite adhesive which is plasticized by water. As a consequence it acts as a constraint leading to high stresses at the interface which weakens faster. C.D.M. Liljedahl et al. in [65] and I. Hopkinson in [66] reports that mechanisms of water ingress occurring in a multi-material adhesive joint are different where compared to those found in a bulk adhesive, with water ingress progressing much faster in joints. In this case the water uptake becomes linear with time, not anymore proportional to the square root of time like for the Fickian diffusion model.

M. Eftekhari and A. Fatemi in [67] noted that reinforcing fibers used in composites are considered hydrophobic, since they absorb far less water than the polymeric matrix, but at the same time, they work as preferential paths for moisture penetration. Moreover, A.Q. Barbosa et al. in [68] stated that hygrothermal ageing depends on the nature of the fibers and additives used to promote fiber/matrix interface; the debonding of fibers from the resin causes a reduction of stress transfer between the two parts, leading to a loss in terms of the mechanical, thermal and physical properties. For what concerns the polymer matrix, evidences from X. Jiang et al. in [69] and T. Dai and H.L. Dai in [70] showed that the adhesive resin is more susceptible to temperature-moisture coupling effect than composites: the elastic modulus of the adhesive material was found to decrease almost linearly with the moisture content and accentuated by elevated temperatures.

Furthermore, when moisture problem is considered in adhesive joints, it is important to consider every contribute of ageing: in fact, moisture is absorbed by adhesive joint both during pre-bonding and post-bonding phase. The first risk of moisture absorption occurs during manufacturing or maintenance process in case of repair, when the bonding between adhesive and substrate is setup. Risk of moisture contamination is present during material storage, transportation, manufacturing treatments, repair on field, where the material can be exposed to humid environmental conditions, leading to a loss of joint strength and fracture toughness, or it has already undergone ageing during previous operations in service. During pre-bond phase, moisture penetration leads to plasticization, new voids, reduced interfacial adhesion, which induce further degradation and performance drop during adhesive operations. J. Mohan et al. in [71] present the solution to mitigate moisture absorption during pre-bonding. The technique

consists in drying the substrate and cure the adhesive joint at controlled hydro-static pressure, which also boosts mechanical properties, especially joint strength. Post-bond moisture uptake occurs in the adhesive joint by diffusion, during operations: it depends on several parameters (adhesive/adherent material, bonding method, working conditions, time of exposure) and lead to a reduction of joint strength due to weakened fiber/matrix and adhesive/substrate interface bonding. [55,61].

In aeronautics adhesive bonded joints are used to restore structural integrity of damaged structural parts but their durability in humid environment can be reduced in time. Hygrothermal cycles caused by repeated altitude changes during flights could further deteriorate the joint strength and lead to premature failure of the structure. S. Budhe et al. in [61] showed that the use of bonded repairs brings significant advantages in terms of maintenance costs, with respect to replacing the component; it represents a quick and flexible solution to repair damages. Moreover, they stated that to reduce a/c downtime, these repair methods can be implemented on field (“cured-in-place” approach), away from the facilities, though imposing strong technological limitations in terms of available equipment and curing procedures and increasing the risk of environment contamination [61]. Composite joint patches for repairs have a higher service life with respect to standard metal joints, as assessed by different immersion tests, which highlight improvements with respect to the un-repaired case, increasing the fatigue life up to 50% and a number of cycles to failure increased by ten times. The high stiffness of composites allows higher stress transfer between the cracked plate and the composite patch throughout the adhesive layer. During ageing their service life is still higher, but for longer times the advantage of composite joints in terms of life extension expires. The reduction of fatigue life due to water absorption attenuates the performances of the composites patch as showed by B.B. Bouiadjra et al. in [72]. Once again, this consideration shows how relevant is the time variable in hygrothermal ageing problems. Due to safety concerns and strict normative, especially for aerospace, marine and offshore applications, the widespread use of adhesives for repair is still limited to secondary structural components and further developments are needed in this field to assess the long-term behaviour in humid environments [61].

3.3. Wind turbine

Composite sandwich panels and adhesives are used in several industrial applications, including some particularly affected by humidity presence, since their operations are performed in harsh environmental conditions, where humidity is very high, like coastal wind turbine blades, or they are even submerged, as in the case of tidal turbine blades. Hygrothermal ageing is a significant problem for wind turbine installations, especially near the sea (coast, offshore), because of the substantial exposure to very humid environments and due to the morphology of the turbine blades. In fact they are produced in order to be as light as possible, to maximize the efficiency: to achieve this goal the internal part of each blade is hollow or contains a very porous filler with a very low density, like foam or balsa, which are prone to accumulate humidity and water [32].

Rocha et al. in [32] analyzed the response of wind turbine blades to diffusion and hygrothermal ageing. Water absorption damage analysis, is performed through immersion tests followed by static and fatigue tensile tests, which are carried out on the sole resin specimen and on the whole composite. The comparison of mechanical properties variation shows a reduction of shear strength of 17% for the sole resin, 36% for the composite. The loss of mechanical properties is significantly greater in case of whole composite, which indicates that the fibers play a fundamental role in contributing to the reduction in performance, during an ageing process, because the interface formed between the fibers and the resin is subjected to strong moisture aggression. Another comparison of mechanical properties is made before and after dry conditioning. Resin

only showed a complete or nearly full recovery, with only a slight reduction of failure strain, while composites show a partial recovery of strength and shear stiffness. Such a different behaviour is explained by different hygrothermal ageing mechanisms involved: swelling for resin, damage at the interface for composite (hydrolysis, bond breaking, deterioration of fillers with secondary effects). In other words, as explained by B.C. Ray and D. Rathore in [33] the level of mechanical properties deterioration depends on which type of process occurs: only physical (generally reversible) or also chemical (often irreversible, persistent after drying). Humidity absorption in composites follows Fick's law for short exposure times leading to resin volume changes due to swelling from plasticization, while, for longer times, secondary effects occur such as interface breakage, leaching, polymer relaxation (viscoelastic, non-linear behavior, with gradual reduction of stress in response to constant deformation, i.e. reduced tendency of the polymer to recover its initial shape after load removal), which are often irreversible, due to failure of polymer chains bonds. Fick's law fits quite well the diffusion into the resin; however it shows large errors modelling the behavior of the whole composite, especially for long immersion times, when non-Fickian absorption processes (secondary, irreversible effects) are present [32].

The curves reported in Fig. 5 show water uptake in neat resin specimens and 4/6-ply composite specimens. Neat specimen reaches a higher water uptake with respect to the whole composite ($M_{\%} = 4\%$ for matrix, $M_{\%} = 1,25\%$ for the composite). Composite has a lower water uptake due to the contribution of the fibers, which slow down diffusion: adding fibers, which absorb less water, moisture uptake at saturation is reduced at a fixed weight for the specimens in both cases. On the other hand, the disadvantage induced by the fibers consist in the presence of secondary ageing effects at the interface level, manifested in the long-

term ageing, after saturation, where strong discrepancies between the simulations and the test results are present, while a strong consistency is detected for the resin-only specimen. For this reason, the reduction of mechanical properties for the whole composite is more substantial than for the neat resin.

Then, comparing 4-ply and 6-ply composite specimens, a higher absorption rate (i.e diffusivity, slope of the water uptake curve) is found in the case of thinner composite, so it reaches the saturation earlier.

The main issue of the study is to distinguish between the various effects and contributions to composite performance loss (decouple, isolate irreversibilities from the reversible effects on the sole matrix) [32].

To achieve this goal, it is fundamental to reconstruct the time history of the material by comparing dry/re-dried specimens, resin/composite specimens, before/after mechanical loading action. The presence of irreversible damages can be detected by comparing the mass change between the wet and dry conditions and by doing mechanical tests. The plasticization leads to a reduction of stiffness (i.e. slope) in the composite shear stress-displacement curve, towards saturation. Interlaminar shear strength (ILSS) test shows that, due to ageing, resistance is reduced, both before and after saturation, meaning that time is a fundamental variable to evaluate the damage magnitude. This reduction is explained by: 1) chemical reactions of hydrolysis caused by long-term ageing and leaching of interface material, which causes weakening of interface bonding and the formation of extra voids for further absorption of water; 2) differential swelling stresses at interface level, which promote crack onset and propagation [32]. To isolate irreversibilities, ILSS test on dry/re-dried specimens are carried out. Reversible contribution due to plasticization can be eliminated by drying, while only the irreversible effects remain. Irreversible degradation is also shown by shear

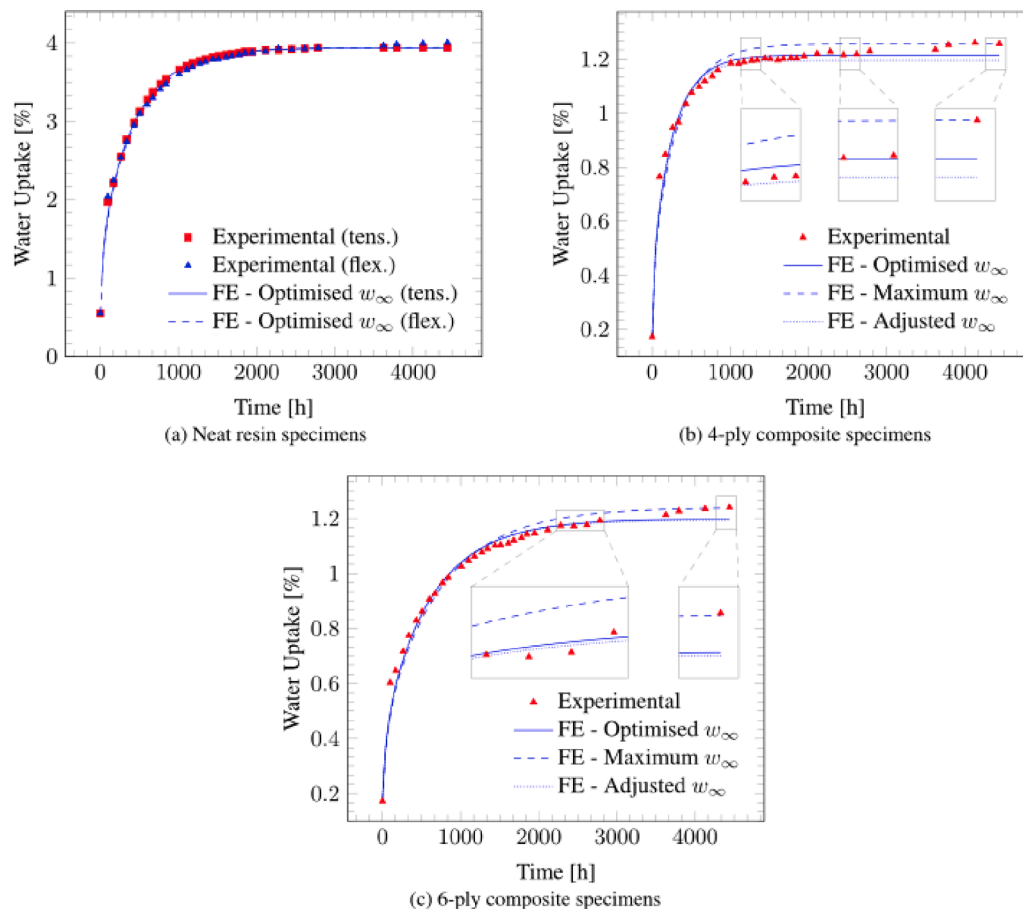


Fig. 5. Water uptake values and Fick's law fit. Adapted from [32].

stress τ and shear stiffness G , which reduce of 20% (irreversibility contribution is significant). Neat resin behaviour after drying is assessed and compared with initial reference conditions (dry); this is accomplished through bending/tensile tests and results show almost complete recovery of stiffness, confirming that irreversible contribution mainly involves the interface between resin and fibers. Further effects on the resin over time, not-recoverable, is detected for prolonged ageing times. In addition, fatigue cyclic tests show maximum shear stress T_{Max} reduction, about 40% (at a fixed number of cycles before failure N). For a given fatigue load, the saturated material fatigue life is reduced of 10^{-3} [32].

Rocha et al. [32] carried out thermal tests on pure resin, to better understand the role of glass transition temperature (T_g) on ageing process. Dynamic mechanical analysis (DMA) shown that at saturation, T_g reduces by 17°C as an effect of plasticization, which is also consistent with the results obtained by the mechanical tests, where a reduction of strength is found after water absorption. Comparing dry condition and re-dried condition, the latter show an increase of T_g of 4°C , explained by secondary effects: after long periods of moisture absorption, irreversible ageing effects occur also inside the resin, where water molecules form very strong bonds with polymer chain molecules (crosslinking, secondary networks with hydroxyl groups, accelerated by additives present in the resin), which permanently alter the free volume inside the material. The effect is an increasing mobility, resulting in a change of stiffness, greater with respect to the initial conditions, and a more brittle behaviour (consistent with an increase of T_g and showing an opposite effect with respect to plasticization, since the chain mobility is reduced by the secondary network).

In conclusion, irreversible composite degradation is only partially explained by alterations in matrix properties (plasticization), largely by secondary ageing effects, which become more and more relevant increasing the exposure time and temperature. With a drying procedure the plasticization is in almost every case recovered, but if water has formed secondary crosslinking that are difficult to remove, these changes become permanent, with only a partial recovery of mechanical properties. Differences between resin and composite behaviour are relevant: while ageing effects do not significantly reduce resin mechanical properties, the response of whole composite is much more evident and, above all, permanent in many cases (mainly at the interface level, with the development and propagation of cracks, with a unrecoverable reduction of strength and stiffness). Differential swelling and interface weakening over time due to filler deterioration are the main responsible of crack formation at the interface, with consequent irreversible damages to the composite structure [32].

D.A. Katsaprakakis et al. in [9] stated that installations in low temperature and high humidity environments, it is essential to avoid or limit the formation of ice on the surface of the blade but also inside the structure, as a result of the freezing of water that has penetrated following moisture absorption. Ice easily clings on the blade surface and acts as a wedge between the sheets, leading to delamination. Once ice is formed on the blade, its removal can be problematic and costly. In fact, ice reduces the maximum load that the blade can bear, so the efficiency is compromised and the blade reaches sooner the operational limits, with a reduction of fatigue life. Moreover, ice alters the blade geometry, with a loss in aerodynamic efficiency and increase in the drag, which is another factor causing the turbine power reduction. In some cases, the presence of ice can cause the turbine to stop, with losses of power produced even up to 20% in the case of installations in particularly cold environments. Then, the expansion of ice during freezing may lead to additional damages to the structure, even bigger than that caused by moisture absorption [9]. These considerations lead to the need of carefully choose turbine installation position: it should be a place where the environment effects are not too harsh and aggressive. If this is not possible, solutions to face aggression of water like surface treatments and protective barriers must be applied. Since the reliability and the extension of the operative life are of paramount importance in the wind

turbine sector, future developments need identify more efficient materials (both resin and fibers), to maximize mechanical performance and increase component's service life also in harsh hygrothermal conditions, as underlined by M. Abedi et al. in [73]. Best operative strategies to face humidity damages should be able to detect any possible critical issue at its early stage, in order to impose corrective actions and avoid detrimental economic consequences, with increasing costs due to maintenance and repair. Losses in power production can be minimized by monitoring critical parameters using sensors and visual inspections. Automatic control systems could use the structural data to give a rapid and immediate response. Considering that the cost needed to replace a wind turbine blade is around USD 200 000, the greatest care must be paid to the monitoring of the health status of the structure. In addition, each day during which a wind turbine remains inoperative due to blade damage generate income losses ranging from USD 800 to USD 1600. Such esteem highlights the significant impact of wind turbine blade damage to the performance of a wind park and the importance of the economic efficiency in the wind turbine industry [9].

3.4. Tidal turbine

N. Tual et al. in [74] and M. Curto et al. in [75] focused their work on tidal turbine blades made of composite materials. These machines are considered highly critical in terms of water absorption and hygrothermal effects, since the material is totally submerged into the sea/ocean water, being exposed to severe operating conditions, with strong impact on the performance reduction. In addition, this component is working in a dynamic environment, under cyclic loads created by ocean waves, so fatigue life estimation is of paramount importance, since long term effects are the most critical in terms of structure reliability and durability. To this regard, tidal turbines reliability in harsh environments is considered one of the most important aspects to guarantee their profitability.

The mechanism of water absorption in tidal turbine blades follows the classic diffusion process, but with respect to a humid environment like atmosphere, sea water is more aggressive and the damages to the structure can be more relevant and critical for the safety of operations. C. de Zeeuw in [76] highlights that hygrothermal ageing for sea installations in composite material is even more dangerous than in other applications such as wind turbine blades and aviation. In addition, some marine applications use not only simple composite laminates but also adhesive bonded joints, which are extremely sensible to humid environments, so their performance is even poorer if they are placed to work under the sea. A further aggravating circumstance for tidal turbine operations is given by the presence of moving parts (blades) put under water, which suffer from cyclic mechanical loads, combined with prolonged ageing. All these co-factors are critical in terms of worse creep behaviour for the structure and life-time reduction [76]. Cyclic loads acting on the turbine, produced by the natural wavy motion of the ocean water, are additional contribution to the severity of the hygrothermal ageing process. Since these cyclic loads interact with the diffusion process, a coupling between water diffusion and mechanical stresses has to be considered in order to assess and estimate with precision the possibility of damage to the structure. If a mechanical damage already exists inside the structure, it accelerates the water diffusion, which, in turn, increase the structural damage, promoting higher stresses and lower load transfer capability. In addition, the presence of loads acting on the structure alters the free volume fraction inside the material, thus leading to a rapid diffusion of water with a quicker degradation as stated by J.Y. Ye and L.W. Zhang in [77].

3.5. Biocomposites

New technological researches performed by A. Moudood et al. in [78], M. Assarar et al in [79], S.H. Mamanpush et al. in [80] and R.Q.C. Melo et al. in [81] are oriented to find materials less sensitive to water

action, especially in crucial applications like aviation, wind and tidal turbines. At the same time, there is a growing interest for new materials that are not only innovative and high-performing but also economical and eco-sustainable, in alternative to the traditional composites, which are synthetic and derive from a petrol-chemical origin. At the end of their service life, these new materials, also known as bio-composites, can be also recycled and re-used for the production of other new components. Re-usability, reduced consumption and pollution allow also to achieve cost savings [31,79,80,78]. Current materials used for marine application deteriorate overtime and under stressful conditions release micro-plastics (e.g. resin additives) in the marine environment, with consequent damage to the ecosystem. Moreover, cyclic action due to wave motion and presence of salt enhance the removal of substances. So, these solutions are oriented to the preservation of the natural environment by minimizing the use of pollutants and toxic materials. Furthermore, the environmental safeguard is becoming one of the main priorities in the industrial world. [31,81,75].

P. Davies in [82] noted that increasing concern about environmental impact has fostered a transition towards biosourced and recyclable matrix polymers. Indeed, even though polyester and epoxy resins with carbon/glass reinforcing fibers are frequently used in aeronautics and wind/tidal turbine blades applications, they don't represent the only option: in recent years new materials have been tested for these applications and results showed that they can be taken into account as a good alternative to standard materials. In marine applications, standard thermosetting polyester resins (synthetic, obtained from petrochemical industry) can be replaced with thermoplastic ones, like polyamide, which can be recycled at the end of their operational life and used to produce new components but, on the other hand, have some disadvantages like faster degradation in humid environments and more costly and innovative technological process for their production. Polylactic acid (PLA), obtained from corn, is an even better alternative than polyamide, since it is fully bio-sourced and so it is also biodegradable. To overcome production issues as in the case of polyamide, a possible alternative is given by the acrylic resins, since they do not require different production process with respect to the traditional ones [82]. Immersion and mechanical tests on these new resins show a good behaviour and resistance to humidity absorption and also an acceptable reduction of mechanical properties after plasticization which can be recovered with a drying process. Temperature plays a central role in modifying the humidity absorption rate: from experiments done by P. Davies [82], a change of temperature from 25 °C to 40 °C caused a three-times quicker diffusion. P. Davies in [82], basing on preliminary results, concluded that this type of resin appears to be a very promising matrix development for composite marine structures, because of the less tendency to undergo humidity deterioration [82]. Especially this last feature makes this resin a suitable solution for the tidal turbine technology, minimizing risks of loss in performance and fatigue life. Finally M.P. Falaschetti et al. in [83] concluded that the sensitivity of the acrylic thermoplastic resin to seawater is rather lower than that of the epoxy, which instead features many hydrogen bonds and tends to attract moisture easily.

To further reduce the environmental impact of materials, natural biodegradable reinforcement fibers can be adopted too. Furthermore, they can be recycled at the end of their lifetime [82]. Another advantage of natural fibers can be achieved in terms of production process, by exploiting renewable solar energy, with a reduced impact on greenhouse effect and also economic savings, since the energy needed from the whole process is far lower. Various natural fibers have already been studied and their response to humid environment has been assessed. Examples are cotton, flax, corn, hemp, kenaf, bamboo, sisal, and jute. However, compared to the standard carbon and glass fibers, natural fibers are extremely sensitive to humidity absorption (water uptake reaches 13/15% instead of 2/3% for the standard materials), so they need special protective layers and film barriers in order to avoid an excessive moisture uptake, losses in mechanical properties and performance.

While in standard composites the resin absorbs the most of water (glass and carbon fibers are quite hydrophobic), in bio-composites the natural fibers are the component which is most exposed to moisture as stated by N. Sgriccia in [84]. S. kalia et al. in [85] underlined that the hydrophilic behaviour of natural fibers is explained by their origin: in fact, they derive from lignocellulose, which is characterized by several hydroxyl groups, enhancing the attraction of water molecules. Therefore, they need to be protected from the external environment with resin and coatings. The high moisture diffusion rates in bio-composites has been explained by G. Ma et al. [86] and by P. Sahu and M.K. Gupta in [87] through the poor compatibility between matrix and fibers, and by the reduced dimensional stability of natural fibers, leading to swelling and a weaker interface bonding [31,78]. Another disadvantage of bio-composites is that they require innovative production techniques, with high levels of precision; in fact, a maximum attention must be paid in the production phase to minimize pre-bond humidity effects, by setting the correct pressure and temperature during the curing phase and removing as many gaps as possible. Regarding this, M Curto et al. [75] report that an increase of 1% of voids during production cause a reduction from 10% to 20% of mechanical properties, during operations. Then, since natural fibers cannot withstand too high temperature and pressure, a limit is imposed on the resin selection for the composite materials, to avoid a rapid degradation: only thermosetting polymers or thermoplastics with low melting point can be selected, which again impose compatibility constraints [78]. For this reason, a trade-off between eco-sustainability and humidity damages need to be considered for the choice of the material.

Many accelerated immersion tests were worked out [31,79,88], to assess the behaviour of bio-composites to water absorption. The results showed that they suffer strong swelling (Fig. 7) and reduction in mechanical properties with ageing, thus their use in the industry sector is still very limited or only in development phase, since new advancements to maintain high performances during hygrothermal ageing are required to respect the current normative. Application is still limited to non-structural parts and only for short exposures to humid environment. L. Di Landro and G. Janszen in [89] concluded that thermoset epoxy resins still remain the only possibly option for high performance use.

A test was performed by A. Regazzi et al. [31] to study the effects of water absorption on a bio-composite made by a polylactic acid resin and natural (flax) reinforcement fibers. The polylactic acid resin was chosen for its good mechanical properties, availability, a standard productive process and full bio-degradability and recyclability. On the other hand, natural fibers used in bio-composites are extremely sensible to humid environments and the bonding formed at the interface level with the resin is quite weak, enhancing more water penetration and leading to higher water uptakes at saturation and loss of mechanical properties. Immersion tests were performed at different temperature levels and for different fiber volume fraction. The ageing effects can be both reversible (plasticization) or irreversible (hydrolysis and other secondary effects), depending on the ageing conditions (temperature level and immersion time). Results showed that by increasing the fiber volume fraction and the temperature level, the amount of diffusion and irreversible effects increases. The tests showed that until 35 °C and for short immersion times the behaviour was similar to the Fick's prediction, with a maximum level of water uptake reached after a certain time, while for higher temperatures and longer exposure times other secondary effects of the ageing process take place leading to a further increase of weight gain, which is explained by the higher diffusion caused by the generation of new diffusion paths into the composite. A reduction of weight with respect to the maximum water uptake level was detected for an operating temperature of 50 °C and the highest fiber percentage (30%), after 144 h of immersion, which is due to irreversible secondary effects like hydrolysis and dissolution, that remove some substances as a consequence of a prolonged water absorption. A general trend consists in the reduction of mechanical properties by increasing temperature and fiber content, which could be recovered only in the initial phase of the

ageing process, when only plasticization takes place (none of the long-term effects, which are in general not reversible) [31].

As assessed by M. Curto et al. in [75], M. Assarar et al. in [79] and R. Masoodi and K.M. Pillai in [88] flax, jute, sisal fibers, during immersion tests, absorb huge amounts of moisture, leading to a sensible reduction of mechanical properties (Fig. 6), especially if they are present in high volume fraction, as can be seen in Fig. 7.

The behaviour of vegetable natural fibers (like jute) and mineral-based natural fibers (as basalt) with respect to humid environments is reviewed in literature, showing the good resistance to moisture in case of basalt fibers, while natural fibers reinforced composites require at least surface treatments to avoid too high water uptakes. Sisal fibers are considered one of the best solutions for bio-composites, since they show better resistance to humidity than other natural reinforcements, but at the same time show a poor compatibility with the polymer resin, that only surface treatments or special glyoxal phenolic resins can partially improve [87,75]. Comparisons between natural composites and standard fiber-reinforced polymer composites highlight the main drawback of natural composites: long-term durability.

M Curto et al. [75] reviewed the behaviour of glass-natural fibers or carbon-natural fibers hybrid bio-composites in humid conditions, finding compromise solutions: water uptake after immersion tests was reduced with respect to the full natural fibers bio-composites, but still higher with respect to standard composites(Fig. 8).

The new perspectives of eco-sustainability offered by natural bio-composite materials to overcome the actual fossilbased economic system need a further development, knowledge and solutions to keep high the performance of the structures in very humid environments. In particular, they have to take in great consideration potential critical issues that arise if the structure is designed for a marine application [75].

4. Conclusions

This review focused on the description of the major risks deriving from hygrothermal ageing and their effects on the durability of composite materials. Despite the large literature and several studies on the subject of hygrothermal ageing in polymers and composites, it is still considered a challenging research topic, which has not been entirely understood yet. The analysis of case studies from investigations of accidents occurred in the last decades assesses several failures in aircraft structures caused by moisture absorption. This confirm that hygrothermal ageing is a topic which must not be underestimated and requires particular attention and further studies. The reports of previous accidents also showed that some composite structures suffer ageing damages more than others: sandwich panels and adhesive bonded joints are two of the most recurring components involved in failure events. Besides aeronautical sector, these structures have application in wind and tidal turbine blades, which are considered particularly susceptible to ageing damage since they operate in environments with high humidity levels or directly underwater. Bio-composites behaviour in aggressive humid

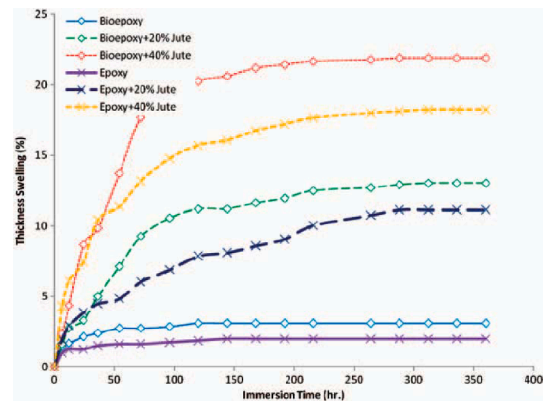


Fig. 7. Swelling by water diffusion: bio-composites with bio-epoxy resin and jute fibers; traditional epoxy composites. Adapted from [88].

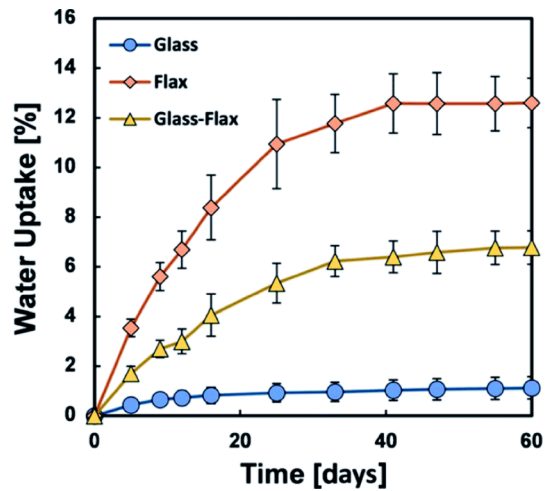


Fig. 8. Enhanced water uptake resistance with the addition of glass fibre into flax bio-composites as a hybrid configuration. Adapted from [90].

environments was also analyzed, leaving safety concerns for their usage for primary structures but, at the same time, revealing their potential as new sustainable and green material for the future, which should be taken in great consideration by industries.

In conclusion, nowadays, the problem of humidity deterioration in composites is far from being completely solved, as demonstrated by recent a/c accidents by the limits to the application of bio-composites and by the lack of effective solutions. Future developments are still needed to implement monitoring systems fully capable to monitor autonomously the behaviour of the structure and its response to humid

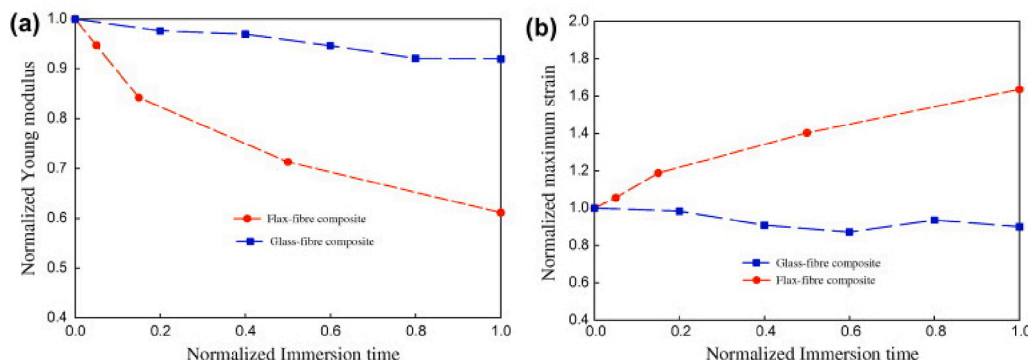


Fig. 6. Comparison between glass-fiber and flax-fiber composite mechanical properties. Adapted from [79].

environments.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

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