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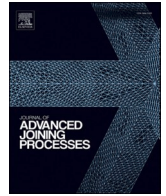
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Accelerated aging procedure of epoxy structural adhesive for marine offshore applications

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ABSTRACT

Knowledge of the long-term performance of adhesive connections is undoubtedly of paramount importance to enable their deployment in civil, mechanical, and other engineering applications. Over time, adverse environmental conditions can strongly influence the performance of adhesive joints leading to a progressive deterioration of their initial mechanical properties. The use of adhesive connections for secondary structures in offshore applications is a technology that allows for the rapid creation of structural members that, however, cannot ignore the influence of hydrothermal effects on mechanical performance due to environmental conditions. In this context, the investigation of the hygrothermal durability of adhesive connections was undertaken through an extensive experimental programme. More specifically, 130 cylindrical steel joints bonded with a commercially epoxy resin for structural applications were tested in Mode I using an Arcan-modified device. Prior to test, the specimens were placed in climatic ovens capable of combining the effects of temperature and humidity for approximately 320 days. In addition, the glass transition temperature, T_g , was assessed by employing the differential scanning calorimeter (DSC) technique to correctly define the experimental ageing conditions. The experimental results show how ageing conditions influence the mechanical properties of the epoxy resin investigated. Finally, some predictive formulations are proposed to calculate the loss of strength of adhesive joints over time.

Introduction

The development of commercial-scale floating wind turbines is set to grow significantly (Petrie, 2013; Weitzenbock, 2012) in the coming years, after several countries in Europe, the United States and Asia recognised them as the best solution for sustainable energy production. Over the years, to join secondary structures (parapets, railings, stairs, pipe supports, electrical cables) to offshore installations, civil and mechanical engineering has used welding or other mechanical joining processes such as bolting or riveting in perforated plates. However, in marine structures, these joining processes are not the optimal solution for reasons of sealing, safety and economy. In addition, the elaborate and expensive process of making or replacing these components is not conducive to the deployment of these key structures for marine renewable energy production.

For these reasons, adhesive bonding (E. Jarry and Shenoj, 2006) is recognised as a viable candidate for offshore structures. Adhesive bonding is expected to provide both better strength properties and time

and cost savings. Furthermore, amongst other advantages, adhesive bonding provides large stress areas, dampens vibration and absorbs shock, minimises or prevents galvanic corrosion between dissimilar metals, joins all shapes and thicknesses and any combination of dissimilar materials, ideal characteristics in the marine environment. In addition, avoiding high welding temperatures leads to safer construction in hazardous environments and makes a positive contribution to preserving and improving the quality of the environment by reducing the amount of weld slag produced.

However, the bonding method employed on land is not investigated enough for marine applications subjected to severe environmental conditions. For this reason, bonding in the marine environment is still in its infancy, despite some successes in other sectors (aerospace, automotive and civil engineering).

To propose reliable solutions, it is essential to be able to guarantee long-term properties and sufficient mechanical resistance. The aim of this study is, therefore, to characterize the mechanical performance of adhesive connections for secondary structures in marine environments,

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including their long-term behaviour. In fact, the long-term durability of joints in marine environments is one of the factors that have limited the more widespread application of adhesives for offshore structures (E. Jarry and Shenoï, 2006; M. Lamberti et al., 2023).

In the literature, several studies have focused on the effects caused by wet ageing of adhesive joints.

Marine environments can be very severe and cause reversible or permanent changes in the mechanical properties (strength and stiffness) with longer ageing times of the adhesive (Xiao and Shanahan, 1997) and substrate/adhesive interface, leading to corrosion, cracking or debonding (Bowditch, 1996). Much work has been devoted to characterising the durability of bonded joints in different sectors (LJ, 2002).

The ageing of materials refers to the change in their mechanical properties over time (Davies and Eppard, 2007) keeping in mind that the properties of interest are those related to the safety and efficiency of a structure.

Due to the difficulty of testing specimens over a long time under ambient conditions, an accelerated ageing procedure must be defined. An accelerated ageing process aims to predict the real-time ageing behaviour of adhesive connections used in marine environments.

This procedure allows the response of a material to be determined under normal conditions of use for a relatively long time, by subjecting the material for a much shorter time to stresses that are more severe or applied more frequently than normal environmental or operational stresses. Another important reason to use accelerated ageing techniques in material qualification testing or assembly is to bring the product to real-world applications.

The acceleration process can be achieved by applying higher levels of temperature, humidity and other aggressive conditions. For example, the impact of moisture content absorbed into the adhesive, at high or low levels, could accelerate ageing damage. Furthermore, the presence of humidity and temperature can influence the behaviour of the adhesive, causing an irreversible loss of mechanical properties.

Additionally, testing may be conducted at a higher than usual level of stress, temperature, humidity (humidity), temperature cycling, chemical environments, salt spray, applied stresses, or other factors.

In the literature, various studies experimentally investigate the performance of unsealed adhesively bonded metal joints in marine environments.

In their research work, Davies et al. (Davies et al., 2000) found that the tensile strength at failure, for adhesives such as polyester and epoxies that adhered to steel, decreased when exposed to real seawater from the Atlantic Ocean (Brest, France). Furthermore, the failure strength was higher under tidal conditions compared to fully adhesive specimens immersed in water.

Alia et al. (Alia et al., 2013) tested polyurethane and vinyl ester adhesives for fibre-metal laminate applications in real seawater from Santander Bay in Spain and determined that water absorption in the joint can be critical. In detail, the authors determined the percentage of water absorption capable of generating an irreversible degradation of the adhesive materials, concluding that for the polyurethane adhesive the ageing conditions led to a loss of stiffness and resistance.

Similar conclusions were carried out by Hayashibara et al. (Hayashibara et al., 2020), asserting that the prevention of water or moisture in adhesive connections (acrylic adhesive), particularly at the adhesive/substrate interface, is important for marine applications (ship decks) to avoid premature failure. Broughton (Broughton, 2012) conducted immersion tests of epoxy adhesives and found that degradation due to moisture ingress is the main cause of failure or damage in service.

Other studies (Ellis and Karasz, 1984) found that moisture in adhesive connections can change the glass transition temperature of epoxy adhesives, leading to significant plasticisation. Over time, seawater penetration into steel adhesive joints caused a significant decrease in strength and, as ageing progressed, the type of damage changed from cohesive to interfacial failure (Bordes et al., 2009).

Horton and Sprinks (Horton and Spinks, 1992) performed

experimental tests on aluminium-bonded connections exposed to NaCl. The results indicated the presence of NaCl as the most dangerous for the durability of bonds between epoxy adhesive and aluminium in marine environments. Similarly, Fay and Maddison (Fay and Maddison, 1990) performed hot shear tests after exposure to salt spray, measuring a reduction in adhesive strength. Other experimental tests on epoxy adhesives exposed to seawater with different salt levels were performed by Rudawska (Rudawska, 2020). In contrast to other research work, she found an improvement in the compressive properties of the epoxy adhesive after ageing due to low salt levels.

Jarry and Shenoï (E. Jarry and Shenoï, 2006) studied the influence of the adhesive thickness on the performance of aluminium/steel joints bonded with acrylate for marine applications. The data showed that the shear strength and stiffness of adhesive connections decrease with increasing adhesive thickness.

However, it is not possible to ignore the moisture absorption behaviour of epoxy resins, the diffusion of which depends on temperature and humidity. The absorption of moisture in the marine environment can produce both chemical and physical processes. Chemical absorption involves the reaction of water molecules with the solid material to form chemical compounds. This process typically involves the dissolution of water molecules in the solid material or the formation of hydrates. Chemical absorption is often irreversible and leads to the formation of new chemical species. Physical absorption, on the other hand, involves the attraction of water molecules to the surface of a solid material through weak van der Waals forces. This process does not involve any chemical reaction between the water molecules and the solid material. Physical absorption is typically reversible and depends on factors such as surface area, temperature and pressure.

Furthermore, in a marine environment, steel structures bonded with adhesives may be subject to corrosion at the interface due to several factors such as exposure to water, electrochemical, crevice and galvanic corrosion, and, finally, the properties of the adhesive.

Marine environments expose structures to seawater, which contains chlorides and other corrosive agents. When water infiltrates the interface between the steel and the adhesive, it can accelerate corrosion processes. If there are discontinuities or defects in the adhesive bond line, leading to accelerated corrosion of the steel. In areas where water can become trapped between the steel and the adhesive, such as voids or crevices, crevice corrosion can occur. Some adhesive formulations may contain components that are corrosive to steel or promote the initiation of corrosion. Furthermore, if the adhesive bond is compromised or fails over time, it can expose the steel substrate to the marine environment, increasing its susceptibility to corrosion. Overall, proper material selection, surface preparation, and design considerations are crucial for minimizing corrosion at the interface between steel and adhesive in marine environments.

However, understanding the mechanisms of adhesive degradation is not an easy challenge and researchers and companies are constantly working on this issue in order to improve the experimental data available in the literature.

In this framework, the authors present an extensive experimental programme to study the behaviour of adhesive connections under long-term ageing conditions. More in detail, 130 adhesive steel connections were manufactured and exposed to the combined effects of temperature and humidity. The experimental tests were performed in Mode I up to a time of 320 days using an Arcan-modified device. Adhesive performance was evaluated for two different ageing conditions in terms of strength and stiffness.

The study focused on the investigation of long-term performance of adhesive connections with the purpose of obtaining mathematical equations capable of predicting the time values, expressed in days, at which a certain percentage of mechanical degradation occurs.

Adhesive joints

Adhesive

A total of 130 cylindrical steel adhesive connections were made using two-component epoxy pastes for structural bonding and connection joints, highly thixotropic and commercially available, called Sicomin Isobond Sr 5030/Sd503x (SICOMIN ISOBOND SR 5030 /SD 503x 2021).

The resin and hardener must be mixed very thoroughly until the yellow-coloured resin and blue-coloured hardener offer visual verification of the quality of the mix. After a time of 24 h at 23 °C, the polymerisation process can be considered complete. The mechanical properties declared by the manufacturer can be found in (SICOMIN ISOBOND SR 5030 /SD 503x) and summarized in Table 1.

The differential scanning calorimeter (DSC) technique was used to define the glass transition temperature, T_g , of the glue studied in the current experimental programme.

Fig. 1 shows the DSC curves of the epoxy resin after the curing reactions. The analysis was conducted with a heating step from 60 to 100 °C at a scan rate of 1°/min.

The glass transition temperature of the epoxy adhesive, which is the subject of this investigation, is 71 °C. It is important to emphasise that the glass transition temperature is an important parameter to take into account in order to correctly determine the conditions of the ageing protocol discussed in detail in the following sections.

Steel adhesive joints

The experimental specimens were manufactured by joining two cylindrical S355 steel elements with diameter of 18 mm through a structural epoxy adhesive. The mechanical properties of the S355 steel material are summarised here: yield stress, σ_y , equal to 355 MPa, Young's modulus, E_s , equal to 210 GPa and Poisson's ratio, ν_s , equal to 0.3.

The samples are characterised by a total height of 64 mm, which is the sum of the adhesive thickness of 4 mm and the two cylindrical steel elements.

The high thickness of the adhesive layer was chosen with a view to a possible application on site, carried out directly by the workers, and not in a specialised laboratory. It is important to underline that, although high thicknesses lead to a reduction in ultimate strength, as has been widely shown in the literature (E. Jarry and Sheno, 2006; Maurel-Pantel et al., 2020; Lamberti et al., 2023a,b), they are more representative of actual on-site execution.

Before joining, the steel surface was thoroughly cleaned to ensure proper adhesion and to mitigate corrosion at the interface between steel and adhesive the accelerated ageing process. Proper surface preparation of the steel substrate with sand paper and acetone to remove contaminants and promote adhesion.

A mounting device was used to achieve coaxiality between the two cylindrical steel parts and to control the fixed total height of the samples. Fig. 2 details the procedure adopted for the bonding protocol.

Firstly, half of the cylindrical specimens (five pieces) are placed in the lower holder (Fig. 2a). Next, the second halves are placed in the upper holder, which consists of two metal pieces secured with steel screws (Figs. 2b and 2c). The upper part of the support can slide on the

Table 1

Mechanical properties of Sicomin Isobond SR 5030/SD 503x.

Property	Standard	Unit Measure	Value
Modulus of Elasticity	NF T 51-034	N/mm ²	4500
Tensile strength	NF T 51-034	N/mm ²	62
Elongation at break	NF T 51-034	%	2.9
Shear strength	NF T 76-107	N/mm ²	13.4

cylinders of the lower device. External cylindrical metal elements enable the upper device to be held in the correct position to achieve the desired thickness of the adhesive layer.

In addition, in order to have a perfect cylindrical glue volume for any sample, several aluminium devices were made ad hoc. The devices consisted of two pieces of aluminium capable of encapsulating the cylindrical elements and were fixed with the use of metal screws (Fig. 2d). The presence of a hole in each aluminium device at the glue layer allows the release of excess adhesive used in the manufacturing process (Fig. 3).

Aim of the aluminium device (Fig. 3) is to ensuring proper application and curing of the adhesive to minimize voids and defects in the bond layer.

Hygro-thermal environments

Accelerated-ageing protocol

The experimental programme developed in this research work aims to study the long-term behaviour of adhesive connections that could be employed to join secondary elements in offshore installations such as barriers, parapets, stairs, etc. (M. Lamberti et al., 2023).

During their structural life, adhesive joints are certainly exposed to an aggressive environment due to the presence of high humidity levels.

The ocean represents a real application scenario for offshore structures. Adhesive connections are designed to build secondary members on the offshore installations, above sea level. In this case, average annual ocean surface temperature and humidity were considered to reproduce similar environmental conditions.

The average annual ocean surface temperature is approximately 20 °C, while the relative humidity recorded at the standard height of 2 metres is approximately 80 % (higher than the average relative humidity on land).

However, in an accelerated ageing process, it is important to pay attention to the set of humidity levels that, combined with high temperatures, could produce moisture levels that are not representative of the expected moisture conditions and cause unnatural physical changes to the material investigated.

For this reason, an accelerated ageing protocol was applied according to ASTM standard F1980-16 (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices. 2021).

It is important to note that the most common practice for including moisture in accelerated ageing protocols is to keep absolute humidity constant as temperature increases.

Some examples of relative humidity percentages that can be set to have a constant moisture content for varying temperatures are given in Table 2 (Table X3.1 of ASTM F1980-16 (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices. 2021)), which provides an understanding of how it is possible to have a fixed absolute moisture content in all temperature domains. In Table 2, absolute moisture is expressed as water content in units of ppm.

The water content is calculated by normalising the absolute humidity (pressure units) to the ambient air pressure and multiplying by 10⁶ to obtain ppm units. The calculated numbers for water content are approximately valid at sea level (pressure close to 1 atm), but change at different ambient air pressures.

Moreover, through the graphs in Fig. 4 (Figure X3.1 of ASTM F1980-16 (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices. 2021)), it is possible to determine for the desired value of water concentration in air expressed in ppm the relative humidity percentage to be set in the accelerated ageing protocol as a function of the selected temperature.

Accelerated-ageing conditions

After a curing period of 7 days, the samples were subjected to two accelerated ageing protocols characterised by the same water

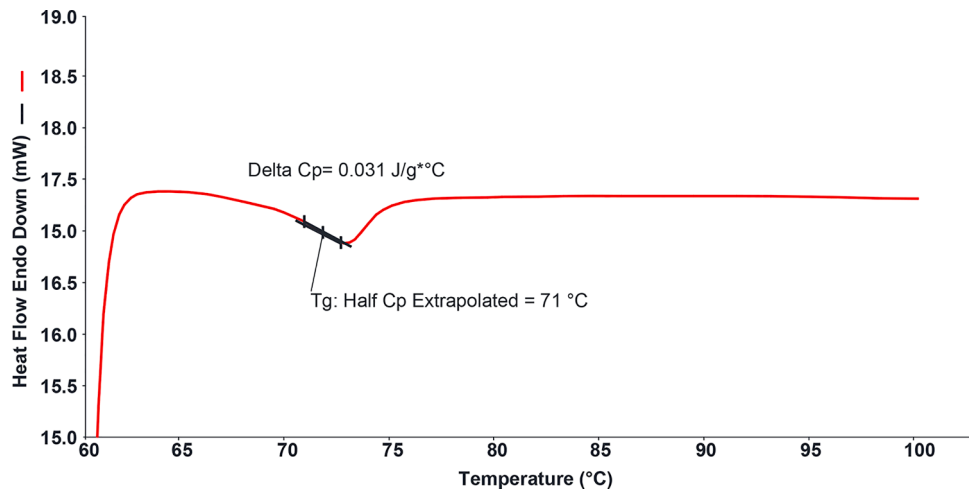


Fig. 1. Differential scanning calorimeter curve for SICOMIN adhesive.

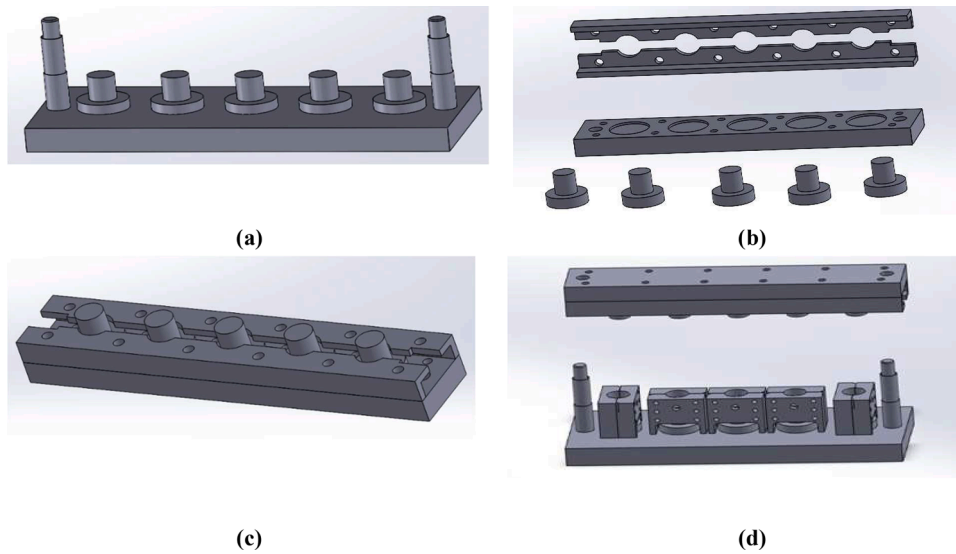


Fig. 2. Procedure for realising adhesive connections.

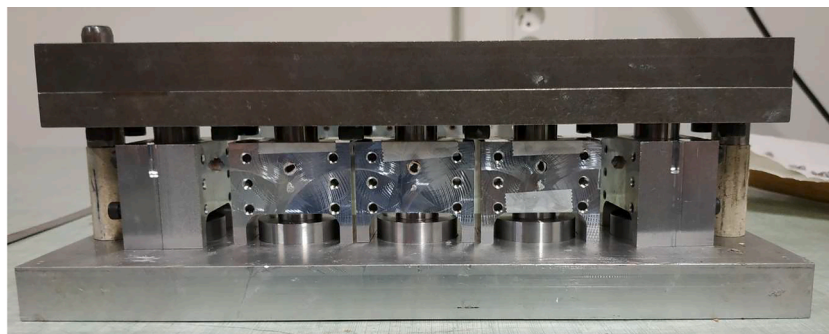


Fig. 3. Preparation of the adhesive joints.

concentration. The temperatures chosen were 42 °C and 35 °C, which were highly compatible with the limitations expressed by ASTM F1980-16 (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices. 2021), according to which the temperature must not exceed the glass transition temperature of the adhesive (indeed, it must be at least 10 °C lower than the Tg). Thus, the temperatures selected were appropriate so as not to affect the accuracy

of the results.

It is important to emphasise that too high temperatures can have a high probability of producing material effects that may never occur in real time or at exposed temperatures.

A relative humidity of 80 % and a temperature of 20 °C (marine environment) produce a water concentration in the air of 18,800 ppm.

According to the graph depicted in Fig. 4, for a temperature of 35 °C,

Table. 2

Example of the relationship of relative humidity to moisture content at a variable temperature (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices, 2021).

Elevated Temperature [°C]	Relative Humidity [%]	Water Content [ppm]
23	50.0	13,750
40	19.1	
50	11.4	
55	9.0	
60	7.1	

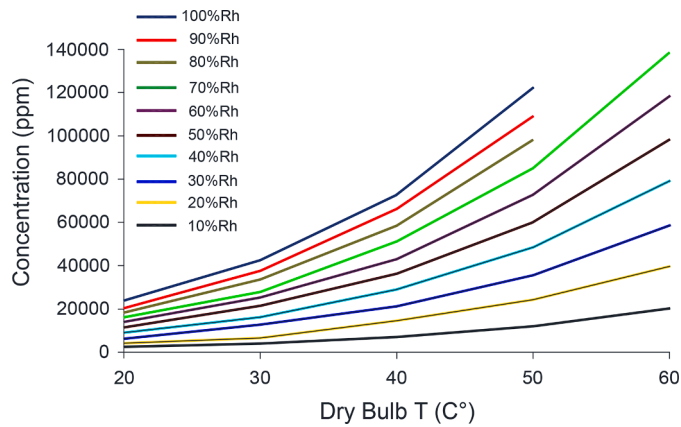


Fig. 4. Concentration of water in air as a function of temperature and relative humidity (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices, 2021).

used for the accelerated ageing process, the relative humidity must be set at 33 % to have a water concentration of 18,800 ppm, and 22 % for a temperature of 42 °C, respectively.

Once the samples were made, they were introduced inside two climatic ovens that allowed two different temperature and humidity conditions to be set (Fig. 5b), as mentioned above. To allow ample heat and humidity diffusion inside the ovens, the samples were placed on aluminium plates characterized by the presence of holes between each placement line manufactured for the actual experimental program (Fig. 5).

Experimental tests

Experimental static tensile tests were performed using the modified Arcan device. The system consists of two half-disks characterized by different attachment points along the perimeter. These attachment

points allow the device to be installed on a standard tensile testing machine. External flanges are used to position the specimen, which are attached with class 12.9 steel screws evenly distributed over it. In order to maintain a good stiffness gap, the vertical half-disks are made of steel and the horizontal flanges of high-performance aluminium. Fig. 6 shows a 3D view of the Arcan-modified device.

Static tensile tests were performed at the CNRS Mechanics and Acoustics Laboratory in Marseille with a universal tensile machine named "MTS 322 test frame" characterized by a load capacity of 50 kN. The tests were performed in displacement control at a quasi-static speed of 1 mm/min. The Arcan device was connected in the clamp of the machine using two ball joint capable of ensuring isostatism and alignment of the applied load (Fig. 7a).

Fig. 7b shows the adhesive layer of a specimen captured at failure during the experimental test thanks the use of a digital camera. As it is possible to note in Fig. 7b the damage evolved within the adhesive layer (cohesive failure).

It is important to note that in the present investigation, only the experimental results referring to the specimens that at failure were characterized by a cohesive fracture were considered and analysed.

On the other hand, the data for the specimens that showed damage at the interface between the steel surface and the adhesive layers (adhesive failure) were discarded.

Experimental results

A total of 16 specimens were tested without the application of ageing conditions to evaluate the initial mechanical properties at time 0. The experimental data are collected in Table 3 where F_u indicates the ultimate force, σ_u the adhesive resistance (ultimate force to the area ratio), δ_u the vertical displacement at failure, and K the global stiffness of the structure.

To evaluate the effect of hygrothermal conditions on the mechanical performance of adhesive joints, numerous experimental tests, about 120, were performed. The tests were performed after different days of exposure to ageing conditions.

The experimental results for the combined effects of a temperature of 35 °C and relative humidity of 22 % are summarized in Table 4 and shown in terms of adhesive strength versus ageing days in Fig. 8, and for the combined effects of a temperature of 42 °C and relative humidity of 33 % in Table 5 and Fig. 9.

As shown in Figs. 8 and 9, for both accelerated conditions applied, at the beginning the effect of higher temperatures with respect to the room environment produces an improvement of the polymerization process (post-curing effects, typical of 2-K adhesive) that leads to an increase of the adhesive resistance between 30 and 60 days. After this period, it is possible to note a slight loss of resistance. Similar results have been obtained in (M. Lamberti et al., 2023; Ortega-Iguna et al., 2022) where properties of the adhesive joints have been increased significantly



Fig. 5. Climatic oven: a) aluminium plates; b) placement of the adhesive specimens.

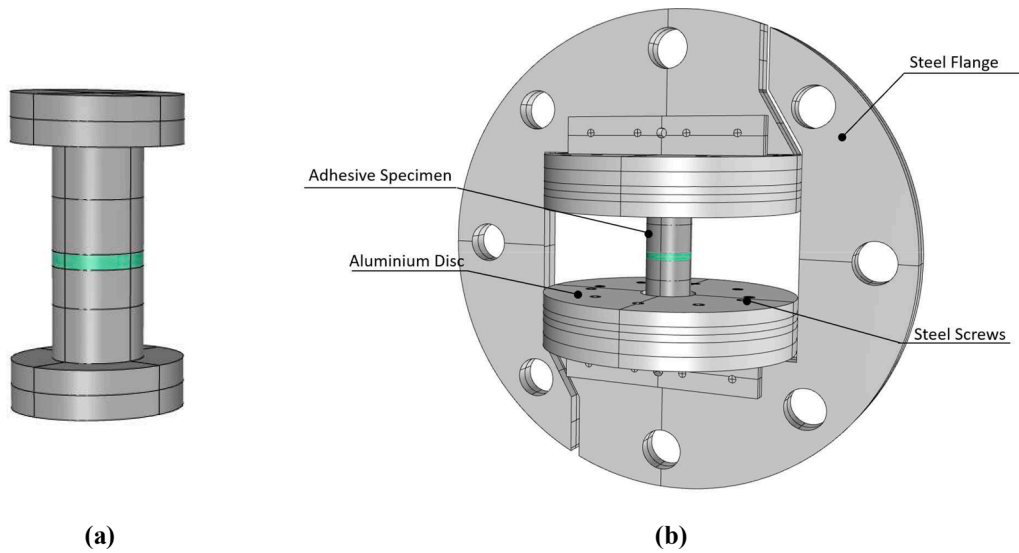


Fig. 6. Experimental set-up: a) adhesive connection; b) arcan-modified device (3D view).

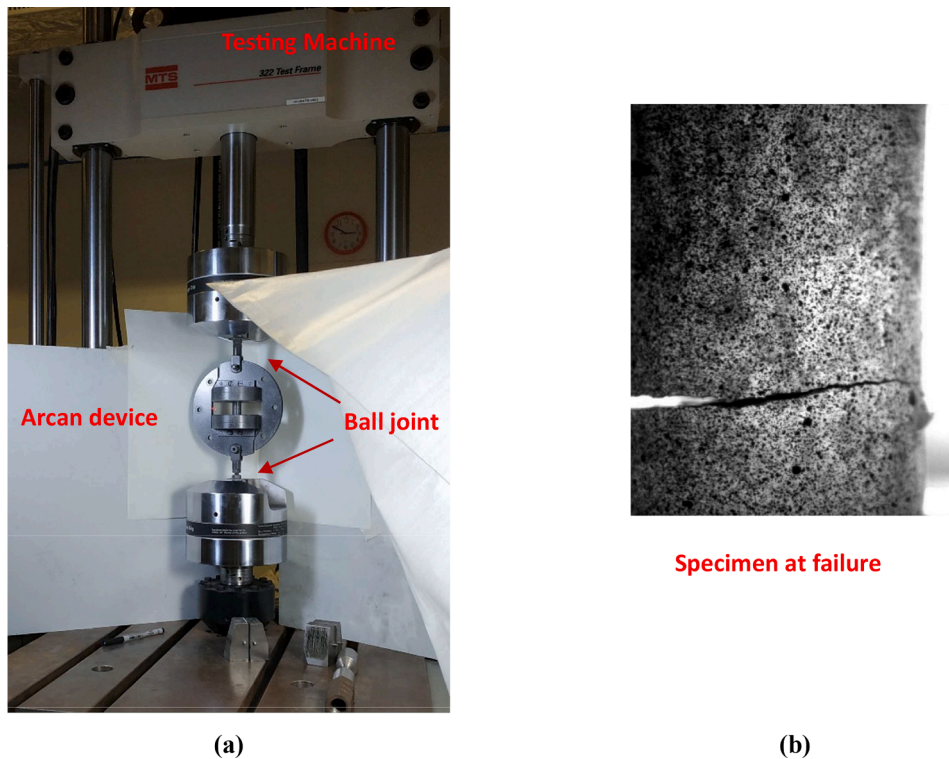


Fig. 7. Arcan device in the MTS 322 universal testing machine: a) tensile tests; b) cohesive failure mode.

during the first month of the ageing exposure.

Although a device system has been used in order to avoid the presence of initial defects, the value of standard deviation reported in Tables 3–5 and depicted in Fig. 8-9 can be explained by the presence of little voids inside the high adhesive layer (equal to 4 mm) generated during two-component epoxy pastes mixture (M. Lamberti et al., 2023). This phenomenon is more evidenced in the first half of the ageing period respect the second one where the reduction of strength caused by the temperature and humidity seems more predominant.

To interpolate the values of epoxy adhesive strength in function of time, an exponential equation has been involved according to the Arrhenius behaviour (more details can be found in Section 6) for the two ageing conditions as reported below:

$$\sigma_u^{th} = \alpha \cdot e^{-(\beta)Time} \tag{3}$$

The two unknown parameters that characterize the proposed model for any ageing condition, α and β , can be calibrated by applying the Mean Squared Error (MSE) minimization technique expressed in Eqn. (4).

$$MSE = \frac{1}{N} \min \sum_{k=1}^N (\sigma_u^{th} - \sigma_u^{exp})^2 \tag{4}$$

where σ_u^{th} and σ_u^{exp} represent the theoretical and the experimental adhesive stress at failure, respectively, while N is the total number of

Table. 3
Experimental results at time 0 (without ageing).

N #	F _u [kN]	σ _u [MPa]	δ _u [mm]	K [N/mm ³]
1	2064	8.11	0.075	109
2	2051	8.06	0.077	104
3	2332	9.16	0.103	89
4	2679	10.53	0.106	99
5	2920	11.47	0.109	105
6	3574	14.05	0.114	123
7	2466	9.69	0.092	105
8	2661	10.46	0.112	93
9	3344	13.14	0.117	112
10	2961	11.64	0.106	109
11	2677	10.52	0.098	107
12	2734	10.74	0.116	92
13	2275	8.94	0.099	91
14	2871	11.28	0.133	85
15	3269	12.85	0.133	97
16	3062	12.03	0.123	98
Average	2746	10.79	0.107	101
Dev.st	429	1.69	0.016	10

experimental data tests.

In the MSE minimization technique, all the experimental data reported in Table 3 (absence of ageing conditions), Table 4 (T = 35 °C and HR=33 %) and Table 5 (T = 42 °C and HR=22 %), are used to define the unknown parameters of the exponential equations (Eqns. (5)-(6)):

$$\sigma_u = 11.17 \cdot e^{-(2.25 \cdot 10^{-4}) \cdot Time} \text{ for } T = 35^\circ C \text{ and } HR = 33\% \tag{5}$$

$$\sigma_u = 11.91 \cdot e^{-(3.68 \cdot 10^{-4}) \cdot Time} \text{ for } T = 42^\circ C \text{ and } HR = 22\% \tag{6}$$

Table. 4
Experimental results of specimen exposed at T = 35 °C and HR=33 %.

days #	F _u [kN]	F _{u,m} [kN]	su [MPa]	su,m [MPa]	du [mm]	du,m [mm]	K [N/mm ³]	Km [N/mm ³]
5	1791	2234	7.04	8.78	0.084	0.088	84	99
5	2163		8.50		0.082		103	
5	2749		10.80		0.097		111	
12	3299	3365	12.97	13.22	0.111	0.118	117	112
12	3430		13.48		0.126		107	
19	2464	2464	9.68	9.68	0.095	0.095	102	102
26	3453	3025	13.57	11.89	0.119	0.106	114	112
26	3350		13.16		0.112		118	
26	2271		8.92		0.086		104	
48	4092	3120	16.08	12.26	0.137	0.107	117	113
48	2210		8.68		0.081		108	
48	3059		12.02		0.104		115	
74	2338	2746	9.19	10.79	0.103	0.105	89	102
74	3155		12.40		0.107		115	
82	3355	3101	13.18	12.19	0.112	0.106	118	115
82	2847		11.19		0.101		111	
88	1861	1861	7.31	7.31	0.070	0.070	105	105
96	2138	2592	8.40	10.18	0.101	0.101	83	101
96	3045		11.97		0.101		119	
111	4391	3339	17.26	13.12	0.149	0.114	116	114
111	2085		8.19		0.075		109	
111	3540		13.91		0.118		118	
117	2743	2913	10.78	11.45	0.107	0.111	101	103
117	3083		12.11		0.115		105	
131	2097	2097	8.24	8.24	0.087	0.087	94	94
152	2392	2526	9.40	9.93	0.101	0.104	93	95
152	2661		10.46		0.107		98	
172	2969	2769	11.67	10.88	0.111	0.109	105	100
172	2570		10.10		0.108		94	
181	2029	2029	7.97	7.97	0.089	0.089	89	89
194	2358	2715	9.27	10.67	0.103	0.116	90	92
194	3072		12.07		0.130		93	
222	2278	2278	8.95	8.95	0.098	0.098	91	91
236	2928	2611	11.51	11.49	-	-	-	-
236	3547		13.94		-	-	-	-
236	2294		9.01		-	-	-	-

It is important to point out that the terms α, being the beginning of the exponential curve, represents the ultimate strength at time 0 (the term Time is expressed in days). The fitting values found from the minimization technique in both cases reported in Eqn. (5) and (6) are perfectly in agreement with the experimental data obtained for the unaged specimens, reported in Table 3, where the ultimate strength is equal to 10.79 ± 1.69 MPa.

Finally, Figs. 10a-b show the stiffnesses of the adhesive connections evaluated from the global mechanical response recorded during the experimental tensile tests for the two ageing cases analysed.

As well as for the adhesive strength, a sensible reduction of stiffness can be noted at varying ageing times.

With regard to the stiffness trend during the ageing time, the beneficial effects of post-curing seem more constant for the first half of both case studies summarised in Figs. 10a-b. This effect can be explained by considering that the global stiffness, K, is an expression of the overall behaviour of the all specimen composed by two steel cylindrical elements bonded together by means of an epoxy resin during the load path. On the other hand, the adhesive stress at failure, σ_u, is the resistant capacity of the only epoxy resin and thus most affected by material degradation processes.

Recent studies (da Costa et al., 2022; Borges et al., 2023; da Costa et al., 2023; da Costa et al., 2021) have highlighted some important aspects related to the interfacial hygrothermal ageing of bonded joints. In particular, experimental tests have shown that the rate of water absorption at the interface is faster than that of the bulk adhesive layer. In the phenomenon of ageing, water absorption can simultaneously weaken the adhesive strength and the adhesion level at the interface, causing a reduction in the strength of the joint.

Water absorption can occur within the interface between the

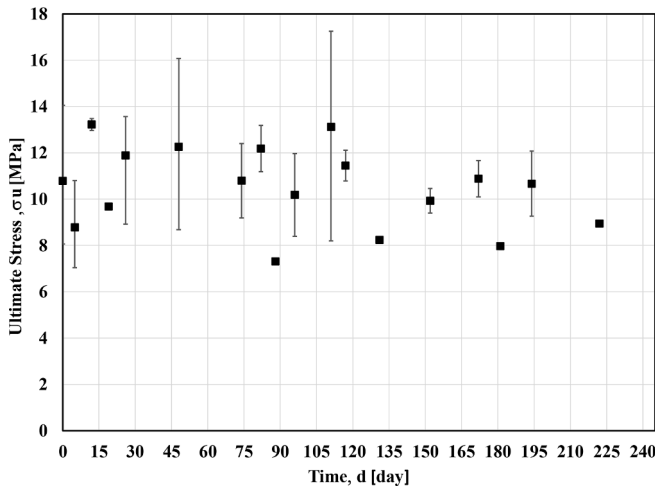


Fig. 8. Trend of adhesive strength of cylindrical bonded joints under accelerated-ageing conditions ($T = 35^\circ$ and $HR=33\%$).

adhesive and the substrate or in the cracks and micro voids in the adhesive layer, leading to interfacial failure of the joints.

Furthermore, it should be considered that in the case of large bonded areas, the rate of saturation of the outer edges is much faster than in the centre of the joints, which may often remain in a dry condition. In this condition, mechanical degradation is a very slow phenomenon over

time.

However, as shown in Fig. 7b, cohesive failure due to the emergence and propagation of cracks was generated for the tested adhesive joints. Experimental tests that showed premature failure or failure of the adhesive interface were discarded.

Undoubtedly, the effects of temperature and moisture absorption in

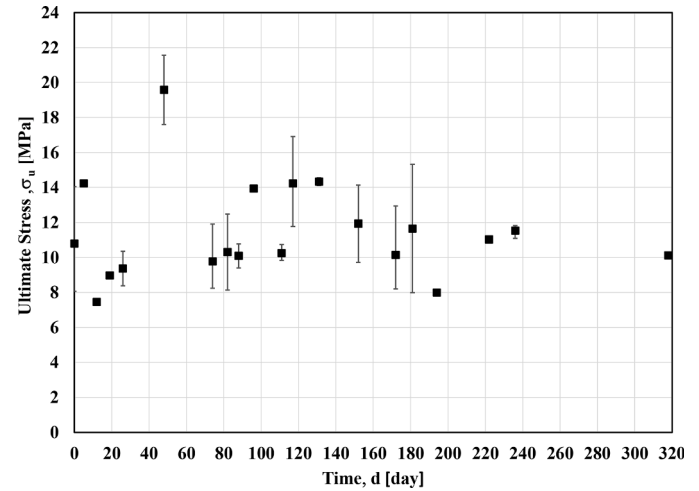


Fig. 9. Trend of adhesive strength of cylindrical bonded joints under accelerated-ageing conditions ($T = 42^\circ$ and $HR=22\%$).

Table. 5

Experimental results of specimen exposed at $T = 42^\circ\text{C}$ and $HR=22\%$.

days #	F_u [kN]	$F_{u,m}$ [kN]	σ_u [MPa]	$\sigma_{u,m}$ [MPa]	δ_u [mm]	$\delta_{u,m}$ [mm]	K [N/mm ³]	K_m [N/mm ³]
5	3622	3622	14.23	14.23	0.130	0.130	110	110
12	1895	1895	7.45	7.45	0.080	0.080	93	93
19	2283	2283	8.97	8.97	0.091	0.091	98	98
26	2132	2383	8.38	9.36	0.078	0.088	107	106
26	2634		10.35		0.098		106	
48	5486	4981	21.56	19.57	0.198	0.179	109	109
48	4476		17.59		0.160		110	
74	3031	2486	11.91	9.77	0.106	0.103	112	95
74	2096		8.24		0.096		86	
74	2331		9.16		0.107		86	
82	2072	2624	8.14	10.31	0.088	0.101	93	101
82	2624		10.31		0.102		101	
82	3177		12.48		0.113		111	
88	2392	2567	9.40	10.09	0.107	0.101	88	101
88	2742		10.78		0.095		113	
96	3548	3548	13.94	13.94	0.121	0.121	115	115
111	2590	2607	10.18	10.25	0.098	0.099	104	104
111	2732		10.74		0.105		102	
111	2500		9.82		0.093		106	
117	2992	3623	11.76	14.24	0.104	0.124	113	115
117	4304		16.91		0.141		120	
117	3572		14.04		0.126		111	
131	3590	3647	14.11	11.93	0.120	0.124	118	116
131	3703		14.55		0.128		113	
152	2474	3035	9.72	10.14	0.098	0.112	99	106
152	3596		14.13		0.125		113	
172	2086	2581	8.20	11.65	0.086	0.102	95	99
172	3291		12.93		0.129		100	
172	2367		9.30		0.090		103	
181	3899	2965	15.32	11.56	0.140	0.118	109	97
181	2031		7.98		0.095		84	
194	2017	2032	7.93	7.98	0.094	0.084	84	96
194	2047		8.04		0.075		107	
222	2806	2806	11.03	11.03	-	-	-	-
236	2822	2933	11.09	11.53	-	-	-	-
236	3006		11.81		-	-	-	-
236	2972		11.68		-	-	-	-
318	2550	2575	10.02	10.12	-	-	-	-
318	2600		10.22		-	-	-	-

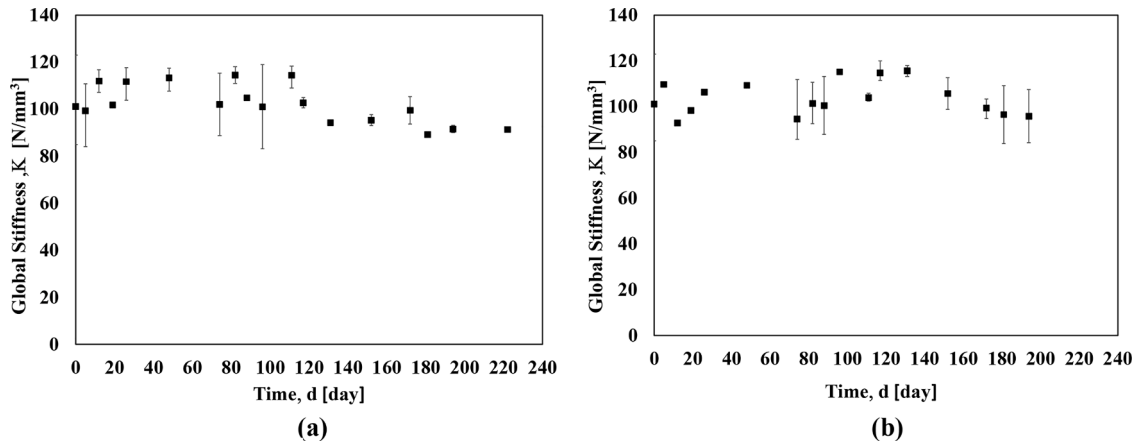


Fig. 10. Trend of global stiffness of cylindrical bonded joints under accelerated-ageing conditions: a) $T = 35^\circ$ and $HR=33\%$; b) $T = 42^\circ$ and $HR=22\%$.

the high adhesive layer produce a reduction in adhesive properties after ageing conditions. In fact, the slightly higher void content that characterises high adhesive joints (in the present investigation, the adhesive thickness is 4 mm) contributes to a higher moisture mass gain.

Furthermore, it is important to remember that both ageing conditions produce the same water content within the adhesive layer according to the applied guideline. This aspect is crucial in order to accurately predict the durability of the analysed epoxy using experimental data derived from two different conditions.

Accelerated-ageing evaluation

The main purpose of the present research is to analyse the long-term behaviour of epoxy adhesive joints for offshore marine applications. To predict the reduction in mechanical strength capacity due to the persistence of environmental conditions over time, an accelerated testing protocol was adopted according to guidelines (ASTM F1980-16 Standard Guide for Accelerated Aging of Sterile Barrier Systems for Medical Devices).

Accelerated ageing techniques are based on the assumption that the chemical reactions involved in the deterioration of materials follow the Arrhenius reaction rate function.

In summary, the acceleration of deterioration phenomena is due to the presence of higher temperatures coupled with well-defined moisture levels in relation to actual environmental conditions.

Importantly, the samples were subjected to temperatures below the glass transition temperature of the adhesive to reduce the risk of the applied procedure leading to premature failure mechanisms that do not occur naturally when ageing is performed at temperatures more representative of the service environment.

As is well known in the literature, the Arrhenius equation is one of the best known models for evaluating adhesive durability and is commonly used to predict the combined effects of temperature and time. It is particularly useful for accelerated tests (short-term tests conducted at elevated temperatures) in order to evaluate long-term exposures at lower temperatures. Using Arrhenius' law, it is possible to ascertain at what point a reduction in the fixed resistance value will occur at a desired temperature.

In the present study, to be representative of possible applications in offshore structures, an annual average temperature of 20°C and a relative humidity of 80 % over the ocean were taken as reference values.

The experimental results, reported in the previous sections, show that aggressive environments can reduce the performance of adhesive joints over time.

Using Eqs. (5)-(6), it is possible to estimate at which days a reduction of 20 % or more in adhesive strength will occur (i.e., 1144 days for $T = 35^\circ\text{C}$ and $HR=33\%$ and 874 days for $T = 42^\circ\text{C}$ and $HR=22\%$). A

similar assessment can be made for a 30 % reduction in strength.

Using Arrhenius' construction (Davies and Evrard, 2007), the kinetics of degradation can be quantified. In more detail, the Arrhenius equation provides the dependence of the rate constant of a chemical reaction on the absolute temperature, as expressed in Eqn. (7):

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \tag{7}$$

where the symbol k indicates the rate constant, A the Arrhenius constant, E_a the activation energy for reaction, R the gas constant and T the absolute temperature.

The Arrhenius equation can be expressed in non-exponential form (Eqn. (8)) which is useful for graphical interpretation also referred to as the Arrhenius construction.

$$\log(k) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \log(A) \tag{8}$$

In this case, time can be associated with the rate constant. The Arrhenius construction consists of a straight line plotted on the logarithmic graph that represents a fixed percentage loss of a mechanical property of interest as a function of the inverse of the absolute temperature.

In Fig. 11 the Arrhenius constructions for 20 % and 30 % of strength adhesive degradation are depicted.

The logarithmic equations extrapolated from the graph allow (Eqs.

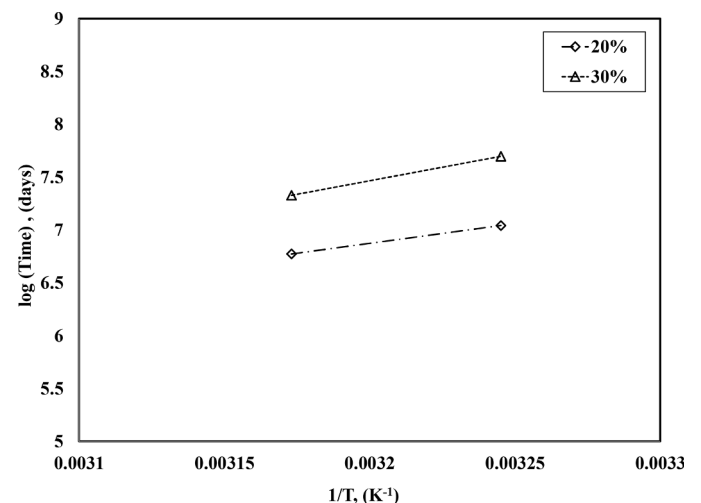


Fig. 11. Arrhenius construction for 20 % and 30 % of strength adhesive reduction.

(9)-(10) to predict at which days the strength degradation reference value will be verified at an environmental temperature lower than the experimental ones set to perform the accelerated-ageing protocol.

$$\log(\text{Time}) = 3737 \left(\frac{1}{T} \right) - 5.08 \text{ for a loss of strength equal to 20\%} \quad (9)$$

$$\log(\text{Time}) = 5129 \left(\frac{1}{T} \right) - 8.95 \text{ for a loss of strength equal to 30\%} \quad (10)$$

Considering a sea temperature of 20 °C, the time predicted for a 20 % drop in strength is around 6 years. On the other hand, if it is considered a drop in strength of 30 % the time predicted is over 14 years.

Moreover, possible application scenarios estimate lower annual temperatures which lead to greater structural life of the adhesive connections considered.

In conclusion, the experimental results encourage the use of adhesive joints for marine applications taking into mind that in order to expand the experimental database should be considered also other factors such as different damage resistance and temperature transitions without forgetting that other types of resins (aramid, polyurethane, epoxy) should be investigated in order to understand their ability to resist long-term effects due to exposure to the marine environment.

Conclusion

A large experimental program on the investigation of adhesive steel connections' performance under ageing conditions has been conducted at the Laboratory of Mechanics and Acoustic in Marseille (France). The specimens were subjected to hygro-thermal ageing conditions for around 320 days before being tested. A monotonic traction load has been applied utilizing an Arcan-modified device to evaluate the strength of the connections on different days.

The results of the study support the following conclusions:

- 1) An acceleration ageing protocol has been applied to adhesive steel connections in order to investigate the long-term performance. The transition glass temperature has been captured through the Differential Scanning Calorimeter technique to avoid applying temperatures that could produce premature failure and not real ageing effects.
- 2) Experimental results show that the effect of temperatures at the beginning of the ageing process improves the curing reaction by increasing the strength of the adhesive samples. This phenomenon was verified for two selected temperatures above room temperature, 35 and 42 °C, respectively. After 60 days, a slow degradation mechanism of adhesive strength begins.
- 3) Experimental data show that adhesive connections do not suffer the loss of mechanical properties due to ageing conditions in a short time. Considering an ambient temperature of 20 °C and a relative humidity of 80 %, the expected time for a 20 % drop in strength is 6 years, while the expected time for a 30 % drop in strength is more than 14 years.
- 4) The experimental results encourage considering adhesive connections for secondary structures as a suitable tool for the marine environment. However, it is important that the experimental database have to be expanded. Going forward, other types of adhesives (epoxy, polyurethane) with different mechanical properties will be studied and long-term mechanical performance will be compared.

CRedit authorship contribution statement

Marco Lamberti: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Aurélien Maurel-Pantel:** Writing – review & editing, Visualization, Supervision,

Methodology, Investigation, Funding acquisition. **Frédéric Lebon:** Writing – review & editing, Visualization, Supervision, Resources, Methodology, Funding acquisition.

Declaration of competing interest

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Data availability

Data will be made available on request.

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