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Evaluation of New Composite Materials for Marine Applications

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Abstract :

Fibre reinforced composites are widely used in marine structures, from small boats to tidal turbines. However, there are some specific features of the marine environment, notably continuous contact with seawater and hydrostatic pressure loading, which require special attention during material selection and design. This paper first describes test procedures developed over the last 30 years to address these conditions in order to identify and validate lifetime prediction models. Surface vessels and underwater applications are discussed. Then, considerations for future applications are described, with particular emphasis on sustainability and environmental impact.

Keywords : Seawater aging, Hydrostatic pressure, Durability, Sustainability

Introduction

Continuous fibre reinforced composites have now been used for marine structures for over 50 years [1-4]. They generally provide excellent specific properties, a range of manufacturing options to produce complex shapes, and reasonable cost, but they can also show some weaknesses. The latter include sensitivity to the environment, the need for more extensive property characterization than metals, a strong dependency of properties on manfacturing conditions, and a risk of delamination due to their laminated structure.

Over the last 30 years the Materials Laboratory at IFREMER, the French Ocean Research Institute, has been involved in a large number of projects to assess the suitability of composites for different marine applications. As a result, considerable experience has been acquired. This paper will describe some of those projects and present the test methods developed to provide laboratory simulations of durability under a range of service conditions. In some cases these were supported by results from tests at sea. The aim is both to provide information on testing protocols and to help the reader to avoid some of the mistakes made in the past.

The paper is structured in three main parts. In the first, surface vessel applications of composites will be discussed. These include boats, ships and infrastructure (e.g. buoys), and represent the majority of marine composite use today. In the second part, underwater applications will be presented. This introduces new loading conditions, hydrostatic pressure in particular, which require special test equipment. The low weight of composites in water is a distinct advantage, but the dominance of compression loading can limit applications. Other underwater applications of topical interest include marine renewable energy (MRE) systems such as tidal turbines. In this case fatigue may be the main design criterion, as damage caused by waves, currents and turbulence loads accumulates. The evaluation of underwater composites applications for the Oil & Gas industry will then be briefly described. In both these sections the materials and manufacturing methods will be described first, from traditional composites through to current developments, followed by discussion of aging tests, structural testing, and in-service experience.

The third section is focussed on future applications, for which sustainability, reduced environmental impact and material recovery at the end of service life will be essential. The composite materials considered for these new applications include biosourced and biodegradable matrix polymers and these require specific durability test protocols. The scope of the paper is limited to continuous fibre reinforced polymer matrix composites, but this covers most of the load-bearing marine applications today.

Composites for surface vessels

Small boat hulls were among the first structures to be moulded from composites in the 1930's and a thriving pleasure boatbuilding market developed in post-war Europe. Today this is a multi-million euro industry in Europe, employing over 80 000 people, of whom 97% work in SME's [5]. Around six million boats are kept in European waters. A large majority of small recreational boats are made from glass reinforced composites, and their design (up to 24m length) is covered by the ISO 12215 standard [6]. This document, based on the extensive experience of certification societies, provides design pressures and stresses and basic material data for design.

There is increasing interest in composites for ships, and various EU projects, both recent (RAMSSES [7], FIBRESHIP [8]) and ongoing (FIBRE4YARDS [9]), have developed large demonstrator structures such as composite decks, rudders, helidecks, hulls, modular cabins and superstructures.

There has also been interest from the energy sector for the use of composites [10,11]. Their corrosion resistance can be attractive on offshore platforms, though fire resistance must be considered. Marine energy applications such as floating and fixed offshore wind turbines rely on very long composite blades; these have shown their value for land-based turbines, but one of the issues to be addressed is the end of life options for the very large quantities of composite needed to meet current targets. The EU is aiming for 300 GW by 2050, which will require around 60000 Tons of composites (based on around 65 T for each 15MW turbine blade).

Materials and Manufacture

When the Ifremer Materials laboratory was set up in the 1980's the main material of interest was glass fibre reinforced polyester produced by hand lay-up. This was used for pleasure boats, military vessels and other industrial applications. Reinforcements were mainly chopped strand mat, woven rovings or a combination of the two. Fibre contents were generally low, around 30% by volume, and high levels of porosity were not unusual. Indeed, an exercise to evaluate composites produced in different boatyards revealed void contents up to 10% [12]. Remarkable progress in materials and manufacturing has followed; on the matrix side we have seen the introduction of special formulations to reduce styrene [13], the use of vinylester as an improved durability matrix [14] and gradually more extensive use of a range of epoxy resins. Today there is increased interest in thermoplastics [15-17]. The Elium™ acrylic range, introduced by Arkema in 2014 is one example [16], a liquid thermoplastic which can be infused so that boatyards can continue to use proven technology. Seawater aging studies have shown comparable durability to marine epoxies [17] and the resin can be recovered at the end of life. Recyclable epoxy formulations are also now commercially available [18-19], based on cleavable amine hardeners so that the resin can be recovered using moderate temperatures (around 80°C) and mild solvents. These recent developments offer a much wider range of end-of-life options [20]. E-glass fibres remain the most popular reinforcement but the number of available forms has extended, with stitched non-crimp fibres and hybrids alongside the traditional woven glass fabrics.

Manufacturing has also moved on, from hand lay-up to vacuum moulding, widespread use of infusion, and RTM (resin transfer moulding) for higher volume parts. This has resulted in safer working conditions and higher fibre contents (50%), but porosity can still be a problem, and preimpregnated reinforcement remains the reference material or performance. 3-D printing is making inroads [21] but has so far been limited in most cases to non-structural parts (its initial scope).

Seawater ageing

In order to establish the extent to which a particular composite can resist seawater ageing the procedure appears simple: immerse a large number of specimens in water at room temperature and remove some periodically to test. Indeed this was how the first tests were performed. However, it is a time-consuming way to confirm that most well-made composites are not very sensitive to water, at least at normal seawater temperatures. In order to be able to predict a 20-year lifetime a change in behaviour must be measured in a reasonable time; it is therefore necessary to accelerate these tests, and the easiest approach is to heat the water. There are standard test methods for absorption such as ISO 62 [22] but they provide little detail on the equipment required. The first accelerated test set-up at IFREMER involved small bench-top 10-litre tanks filled with tap water and heated by electric resistance coils. Loss of water due to evaporation was limited by topping-up regularly. Some early tests revealed rapid degradation of materials, attributed to changes in the water composition due to leaching from samples (acidity) and it became clear that larger tanks with circulating water, preferably natural seawater, were needed. A first concern with accelerated testing (elevated water temperature) is to establish to what extent you are able to maintain water tank temperature within acceptable limits (e.g. ±1°C) for months or years. This clearly requires a water mixing device, continuous temperature measurement and a recording system. Second, if the water is not renewed its physical properties will change with time, so a system which renews water regularly is necessary. Another important question is whether it is necessary to immerse in natural seawater or whether tap water or distilled water suffice. In general, experience has shown that the water composition does affect diffusion kinetics; seawater enters polymers more slowly than pure water [23]. A third consideration with respect to natural seawater is biological activity. Unless distilled water is available for comparison it is difficult to evaluate the influence of parameters such as temperature and pressure. This will be discussed in the final section of the paper below.

A dedicated seawater aging facility was set up at IFREMER in the late 1990’s, Figure 1. The low pressure part of the facility involves a set of 15 large tanks (from 80 to 600 litres), each with a heating system, water renewal and temperature recording. The majority are supplied with natural seawater from the Brest Estuary, but four are filled with de-ionised water at different temperatures, for comparison.

Figure 1. Seawater aging facility, low pressure tanks

This set up has been employed in many projects and data from immersion tests lasting over 10 years have been measured. These provide the possibility to validate (or not) the use of temperature to accelerate tests. For example, Figure 2 shows gravimetric data from a tidal turbine project in which samples of carbon/epoxy of different thicknessses were immersed in 2012. Some of these samples, in tanks at 25, 40 and 60°C, are still immersed after 12 years. Figure 2 shows an example of weight gain measurements for carbon/epoxy prepreg composites. This unique set of data reveals a number of features of diffusion behaviour.

While immersion at 60°C resulted in degradation after 2 years, the weight gains of samples immersed at 20 and 40°C are still quite stable. For this composite material and cure conditions an extrapolation from the accelerated test data would tend to underestimate the material lifetime, as the mechanism leading to a weight increase at 60°C was not observed after 12 years at 25°C, a more realistic seawater temperature, nor at 40°C.

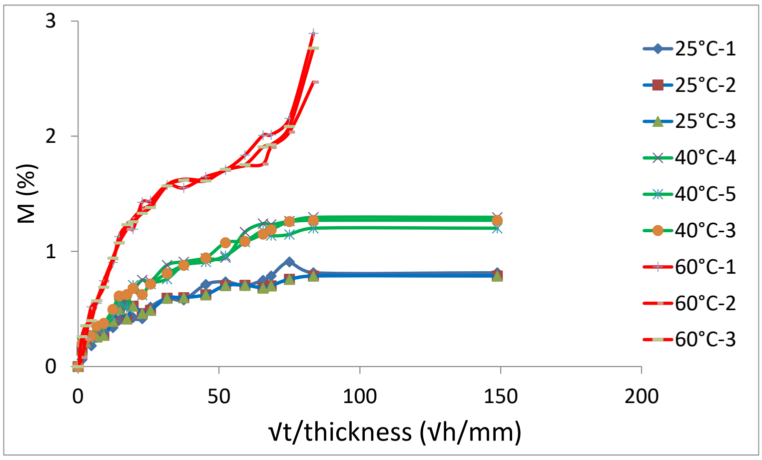


Fig 2. Weight gain plots for 2mm thick prepreg carbon/epoxy coupons immersed in seawater for 12 years at different temperatures.

It should be noted that in order to ensure the reliability of weight gain measurements a robust weighing protocol is required. During long immersions the operators are likely to change, and it is important that care is taken to follow the same operations (from removal from the tank to weighing) as water will evaporate. The weighing equipment must also be calibrated regularly. Once the diffusion data have been obtained it is usually possible to fit them to a diffusion model (Fick, dual Fick, Langmuir…[24-26]) which allows the water profile within a structure to be calculated. This water content can then be related to a mechanical property of interest, in order to estimate the change in the mechanical response of the structure with time, Figure 3.

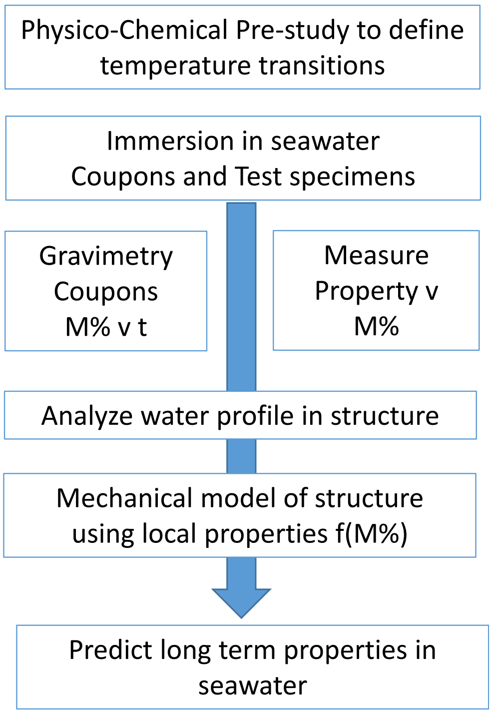


Figure 3. Schematic simplified approach to lifetime prediction after seawater immersion

It should be emphasized that this is a simplified flow diagram and that composite lifetime prediction is not a trivial exercise. When a new material is to be investigated a thorough physico-chemical study is essential, in order to examine the temperature sensitivity and assess the maximum water temperature which can be applied. Standard techniques which can be performed on small quantities of material are used, including DSC (differential scanning calorimetry), DMA (dynamic mechanical analysis) and DVS (dynamic vapour sorption). To obtain the gravimetric data will then take weeks or even months. Even a limited mechanical characterization programme will require dozens, or even hundreds of specimens, in order to provide the properties required as a function of water-content. A complete characterization of the orthotropic properties of composites as a function of aging is a formidable task and is rarely attempted. Robin et al show one recent example [27]. The aim was to determine a complete test matrix on both unaged specimens and after saturation. Significant changes in both in-plane and out-of-plane properties were measured after aging. Physical aging can also take place during immersion and may need to be included in the analysis.

While this exercise can be justified in a few large projects, in most cases when the material family is known and a different grade has been selected, a comparative study using a wellknown marine material as a reference and limited test conditions may suffice to check the material and associated manufacturing process.

A limitation of the simplified approach shown in Figure 3 is that it does not account for any coupling effects. Composite marine structures can be highly loaded and there is evidence that moisture effects and loading can be strongly connected. Thus the ingress of water affects damage development and the applied mechanical stresses affect water ingress. This has been shown by several authors in the past, in particular in the work of Weitsman [28]. The coupling can be modelled [29] but these effects are rarely taken into account in design today. This is an important area of ongoing research.

Structural tests

The traditional approach to durability studies is to quantify the effects of physical and chemical degradation processes on small, standard coupons, and then rely on using these data in models to predict the response of structures. However, this approach needs to be validated, as one of the key features of composites is the close link between manufacturing and properties. In the aeronautical industry a variety of structural tests have been proposed in the 'pyramid' testing approach [30]. These include tests on stiffened panels and assemblies, but these are not representative of the loading cases of interest for marine vessels. For example, boat hulls are subjected to wave pressure, while internal bulkheads of fast surface ships are mainly loaded in shear; specific tests have therefore been proposed to simulate these load cases, [31,32] as illustrated in Figure 4.

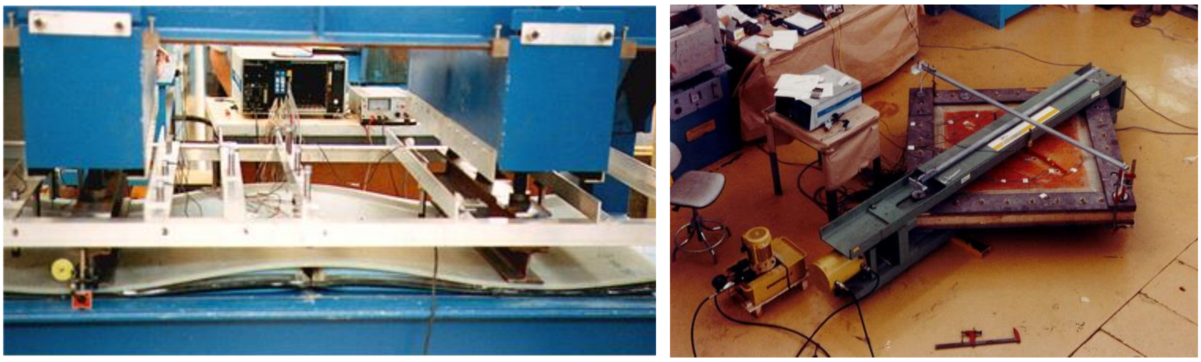


Figure 4. Examples of tests developed specifically to simulate loading of surface vessels,

a) hull pressure loading [31], b) shear of sandwich bulkheads [32].

Dynamic loading is also a concern for fast vessels, which are subjected to repeated impact (slamming) loads. Additional tests have therefore been designed to simulate these [33].

The main added value of such tests, in addition to improving confidence in the proposed structure and verifying the manufacturing method, is that they enable numerical modelling results to be checked in the laboratory at an intermediate scale. Extensive instrumentation can be employed, historically using strain gages but increasingly with digital cameras and image analysis and embedded optical fibers, to provide a wealth of data for correlation. The key to obtaining useful test data is the control of boundary conditions: Finite Element (FE) analysis is widely used, both before the test, to optimize the interfaces between the test fixture and the composite structure, and after testing to interpret the measurements.

In-service experience

Experience with composite boats and ships has generally been very positive. Indeed, the lifetime of glass fibre reinforced polyester MCMVs (mine counter measure vessels) was extended after 20 years' service when studies showed excellent remaining properties [34,35].

Glass reinforced polyester pleasure boats are also extremely robust. It is estimated that in France there are 1 million pleasure boats with an average lifetime of 30 to 40 years. This is partly because most pleasure boats are not used intensively, but they do spend long periods in seawater.

Valuable additional information on service loads can be obtained from instrumentation of full scale composite structures. An example for surface vessels is shown in Figure 5. In this study, a composite motor boat was strain gauged in order to study the deck/hull interface response. It was first studied under controlled conditions in the IFREMER test tank (different drop heights with added weights) [36]. Similar measurements were then made during navigation under different conditions. These full scale tests provided information on the structural response, to use in improved design, and also led to the development of more realistic laboratory testing. Such data can help to reduce the uncertainty surrounding loading conditions and lead to improved material solutions.

Figure 5. Instrumented boat drop in test tank [36]

Composites for underwater structures

The market for composites underwater is still limited, but there have been various projects in the past to demonstrate their potential in two main sectors: underwater vessels (submarines, AUVs, gliders... [37]), and sub-sea oil and gas applications [38]. The latter require 20-year lifetimes, so long term reliability is essential. A third, emerging area is renewable marine energy. For example, tidal turbine blades are permanently immersed and subjected to very high loads, placing very stringent requirements on materials and manufacturing. However, immersion depths are shallow, less than 100 meters, so pressure effects are less important than for the first two applications.

Materials and Manufacture

The most popular material for deep sea structures is carbon/epoxy but for shallower applications glass/epoxy may be sufficient. In order to resist the high pressures to which deep sea structures are subjected these tend to require wall thicknesses of 20mm or more. The manufacturing methods are filament winding or automated fibre placement (AFP). Both can result in defects, either voids for wet winding [39] or overlaps and gaps for AFP [40]. The pressure resistance of the structures will then depend on the sensitivity of the compression behaviour to these defects. Non-destructive testing, by ultrasonic C-scan for example, is an essential part of manufacturing control.

Seawater ageing

First, it should be noted that as the composites used for deep sea structures tend to be thick, tens of millimeters wall thickness, so the time to saturate them with water will be very long. However, water still enters the outer layers and may affect compression properties, and in shallower water applications the structures are much thinner, so water ingress may still be critical. To establish the extent to which hydrostatic pressure affects the diffusion kinetics in materials an additional set of aging tanks was developed within the IFREMER aging facility. Today this includes around 25 pressure vessels of different inner diameters, from 100mm up to 300mm, Figure 6.

a) b)

Figure 6. High pressure aging test facility

For example, the small vessels in Figure 6a were used to perform a set of aging tests on glass/epoxy and carbon/epoxy coupons [41]. This is a specific case of coupling between water ingress and mechanical loading. Figure 7 below shows an example of the results for the glass/epoxy composite. One of the conclusions from this and previous work was that pressure only affects the entry of free water into voids and free volume, not into the polymer molecular structure, at least for pressures up to 1000 bar (equivalent to around 10 km depth). No effect of pressure was found for carbon/epoxy coupons manufactured from prepreg.

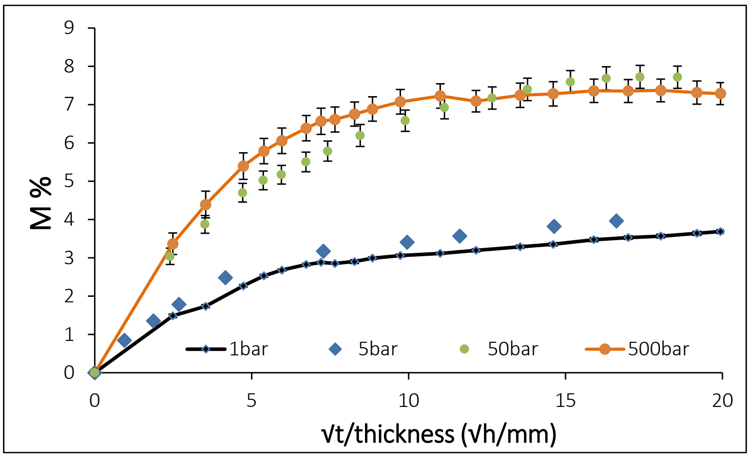


Figure 7. Example of results showing the influence of hydrostatic pressure on diffusion kinetics, glass/epoxy [41]

Arhant et al. [42] studied the influence of seawater aging on the matrix-dependent properties of carbon/PA6 thermoplastic composites. They showed that the compression response of these materials can be directly related to water content. Figure 8 shows an example.

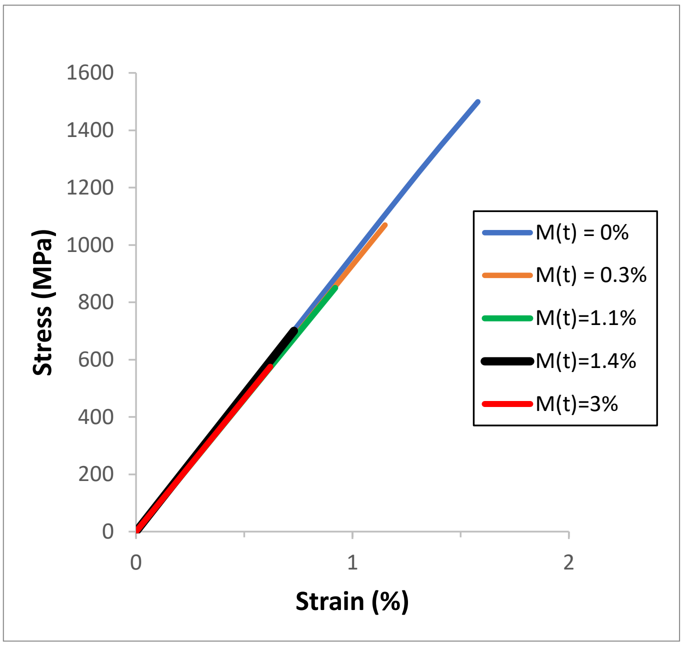


Figure 8. Correlation between compression strength and water content, based on [42].

Structural tests

The hydrostatic pressure acting on underwater structures is directly proportional to the immersion depth. The main structural geometries of interest for underwater applications are spheres and cylinders, and for the latter hydrostatic pressure results in a state of biaxial compression. There is an extensive literature on compression testing of coupons, e.g. [43, 44].

Various papers in the 1990's pointed out the difficulties in conducting valid compression tests on unidirectional composites. These include the sensitivity to misalignment and risk of buckling. Indeed, the current ISO standard on compression testing (ISO14162) includes 2 different test methods. As a result, the approach at IFREMER has been to use hydrostatic pressure tests on tubes rather than axial loading of flat coupons to characterize compression behaviour. This has some benefits; it can avoid coupon edge effects if tubes are tested and the material can be more representative of the thick composites employed. However, it does require more expensive specimens and the availability of a range of pressure vessels with the associated measuring technology. Table 1 summarizes the pressure vesels currently available.

Test type	Maximum pressure, bars	Internal Diameter, m	Length, m
Implosion	1000 1000	1.0 0.6	2.1 1.5
Long term aging	1000 (x10) 400 (x4) 300 (x7)	0.1 0.4 0.2	0.25 1.0 0.8
Mechanical + pressure	10T + 1000	0.15	0.3

Table 1. Pressure test facilities at IFREMER (numbers in brackets indicate numbers of aging pressure vessels available).

Figure 9 shows one example of a pressure test to implosion; a reduced scale composite underwater vehicle was pressurized to failure in a 1000 bar pressure chamber. The first photo shows the steel pressure vessel. The closure plug weighs around 4 tons, the pressure vessel wall thickness is up to 200mm. Often the only information required is the implosion pressure, but if modelling results are to be checked then additional data must be obtained. The specimen may then be instrumented with strain gauges around the central section, which provide information on whether buckling has occurred. For example, Figure 10 shows an example of strain gauge recordings during a buckling failure. This type of measurement requires watertight high pressure connector passages through the pressure vessel cover.

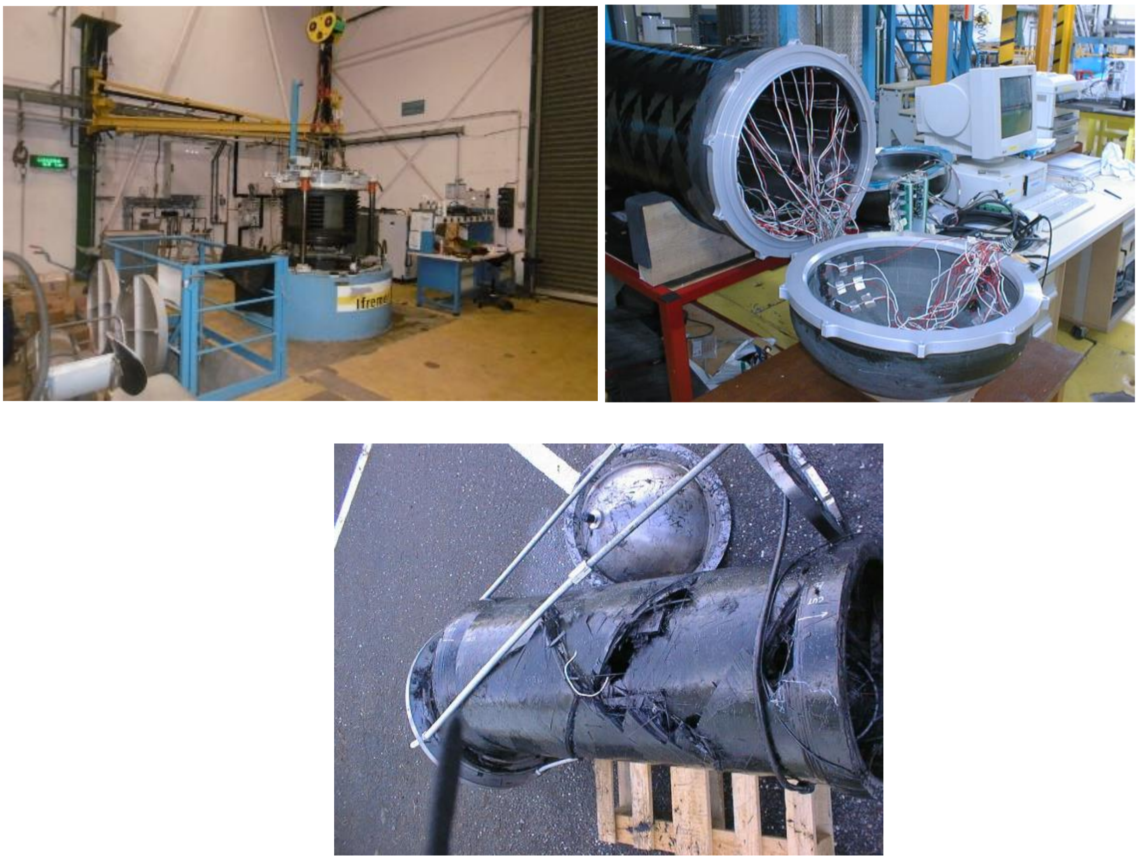


Figure 9. (Left) 1000 bar pressure vessel, (Right) Strain gauged cylinder,

(Lower) Composite cylinder after implosion testing.

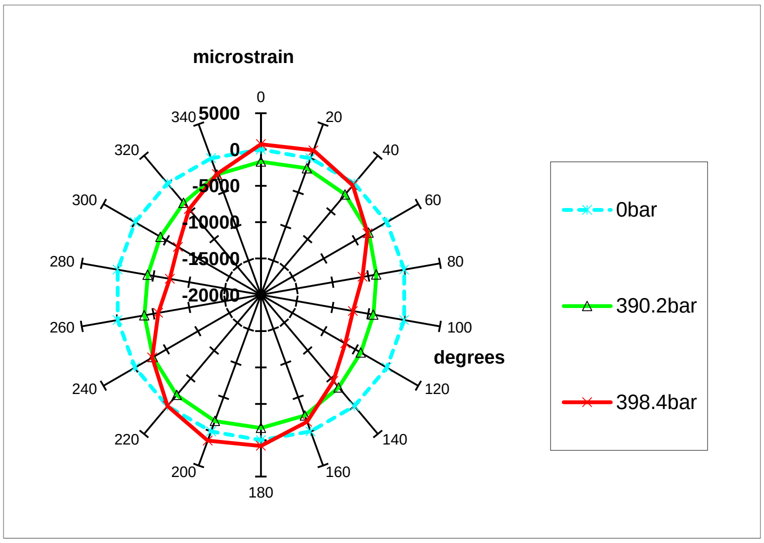


Figure 10. Example of recordings from 18 inner wall strain gages (in microstrain) around mid-section during buckling failure of a carbon/epoxy cylinder.

Implosion tests have also been performed on many composite cylinders in different European and internal projects [45]. Tests on high performance thermoplastic composites such as carbon/PEEK [46, 47] have been followed more recently by the evaluation of lower performance and cheaper matrix composite materials such as carbon/polyamide 6 [48].

In order to observe the effects of pressure directly it is also possible to install special glass port-holes in the pressure vessel, which also allow in-situ image analysis to be applied. For safety reasons these must be proof tested to very high pressures. The influence of pressure on mechanical properties of polymers and composites has been investigated for many years [49, 50]. Figure 11 shows an example of a 1000-bar pressure vessel mounted on a universal test machine for this type of study. It enables standard tests (tension, compression, shear and interlaminar fracture) to be performed under high pressure [51, 52]. After calibration the digital camera provides direct strain data under pressure.

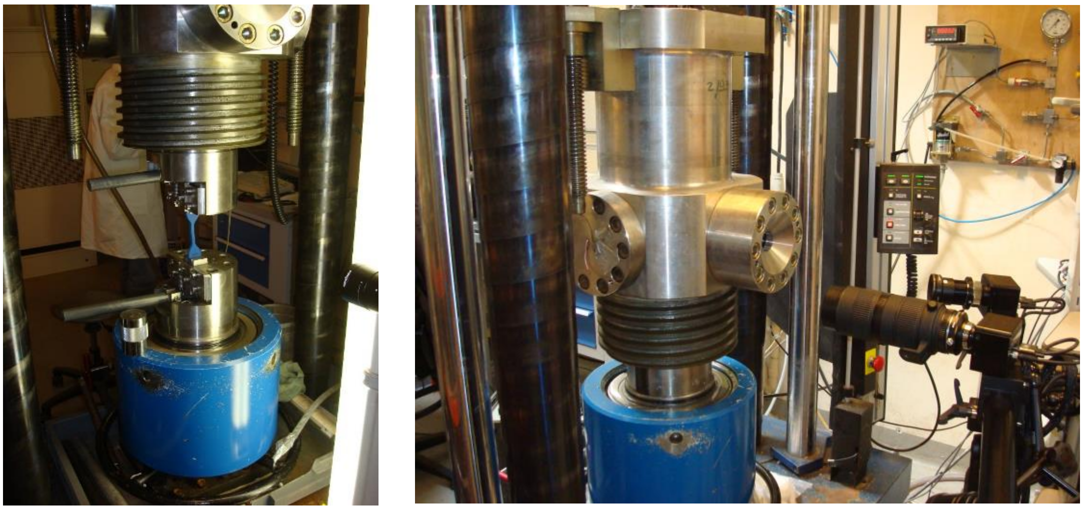


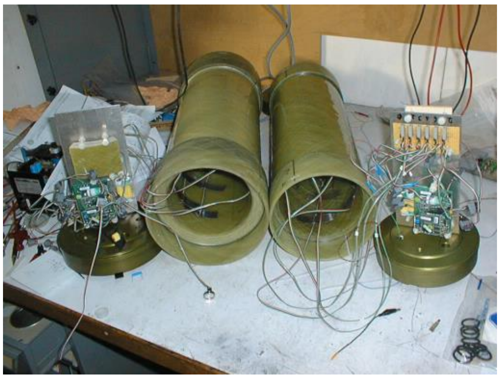
Figure 11. Pressure vessel mounted on universal test frame, open (left), closed (right).

Shukla and colleagues have extended this approach to follow deformation with high speed cameras during tests to failure on composite cylinders [53,54,55].

In-service experience

There is limited published information on military submarine applications of composites. Over 30 years ago Lemière described composites on French submarines, which included decks and sonar domes [38], while Mouritz et al [3] described external casings and fins. However, the latter concluded that certain drawbacks associated with composites, in particular high construction costs, compression fatigue and fire resistance, suggest that it is unlikely that composites ever be used in large submarine hulls. A 2018 overview of manned underwater vehicles can be found at [56]. There are very few manned deep sea submersibles, and while those in service do include composite components (robot arms, protection for syntactic foam buoyancy) the pressure-bearing hulls are metallic.

Composites are used for the protective casings of deep sea oceanographic instruments. One example is autonomous profilers, thousands of which follow ocean currents around the globe. These are basically tubes containing an energy source, a pump and measuring devices to record parameters such as temperature and salinity. For depths to 2500 meters aluminium alloy is used, down to 4500 meters carbon/epoxy is preferred, and developments are underway for a 6000 meter depth composite version. The development programme is based on an AFNOR document for verification of oceanographic equipment, and includes implosion tests and creep strain measurements [57]. Qualification for service is then based on proof tests at 1.2 times maximum service pressure. Measurements at sea of underwater structures can also provide valuable data. For example, strain-gauged glass/epoxy cylinders were immersed at 2400 meter depth at a Mediterranean site, in order to generate long term creep data [58]. Figure 12 shows an example of strains measured over a 2 month period.



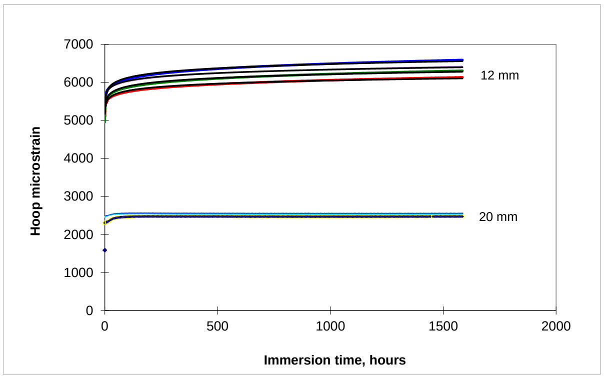


Figure 12. Instrumented glass/epoxy cylinders with data loggers to measure creep strains at 2400 meter depth Mediterranean Sea site with examples of hoop strains for two cylinder thickness, 12 and 20mm (internal diameter 152mm).

The extensive use of composites in the offshore Oil & Gas industry anticipated 20 years ago has not been realized [59, 60, 61, 62]. There were plans for fully composite risers, which reached the sea trial stage, but have not progressed further. Nevertheless composites are being used, in particular for composite pipes, and the experience appears positive [63].

Another underwater example, for marine renewable energy applications, is the instrumentation of the carbon/epoxy composite blades of a tidal turbine, Figure 13. One of the blades was strain gauged, in order to measure its response during sea trials [64]. These structures are subjected to large numbers of cycles, so fatigue data are essential, but in addition to the tidal loads they are also affected by waves and turbulence. Data from tests at sea are essential to optimize blade design. Similar blades were subsequently tested to failure in the laboratory, Figure 14, and the data from measurements at sea enabled more realistic tests to be performed [65].

Figure 13. Strain-gaged tidal turbine blade (with orange stripe) during installation of data loggers to record strain measurements at sea [64].

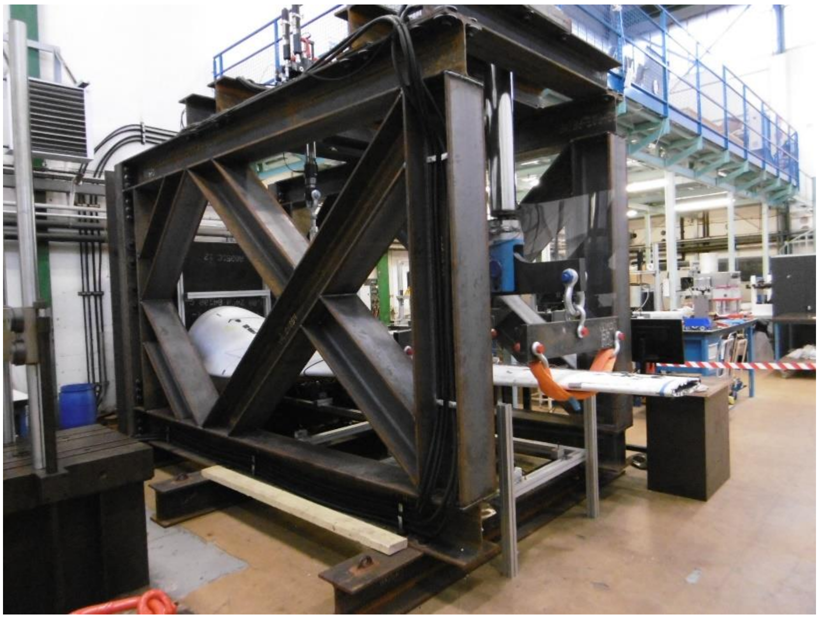


Figure 14. Laboratory test frame built to load to failure 5-meter long carbon/epoxy tidal turbine blades, EU *RealTide* project [65].

Future trends

Composite materials offer improved performance for many marine applications and are today established as a major technology for the marine industry. However, in a context where future materials developments must include considerations of sustainability and environmental impact, the production, transformation and end-of-life characteristics of these materials must also be considered [66]. This will have consequences for the selection and evaluation of new composite materials which will be discussed below.

Alternative reinforcements

One approach to reduce the carbon footprint of composites is to replace the glass fibres with natural fibres. Flax has received most attention to date and there are several features of these fibres which require attention during evaluation for marine applications:

- Variability of properties
- Sensitivity to water
- Non-linear mechanical response.

First it should be noted that these are natural fibres so their properties can vary from year to year according to weather conditions during growth and retting. Baley et al provided an overview of the variability of flax fibre properties [67] and concluded that excellent composite properties with low variability can be obtained. However, this requires control of the the fibre quality, the use of appropriate characterization methods and care with manufacturing processes.

Second, the cellulose in natural fibres has a strong affinity for water. This is revealed as both a significant composite weight gain during immersion, which is proportional to the fibre content, and swelling effects which can result in significant internal stresses [68]. The former include very significant edge effects, as wicking along natural fibres accelerates water ingress. It is therefore debatable whether immersion of coupons in order to establish diffusion kinetics is representative of marine applications such as boat hulls. For this reason there is an interest in using a test which only allows water to enter through the surface, not the edges. One approach is to seal the specimen edges, with silicone for example, but in our experience it is very difficult to guarantee the long term reliability of a watertight seal. An alternative approach is shown in Figure 15a. This presents an aging tank with side windows, onto which specimens can be clamped with an O-ring seal. The coupons are only exposed to water on one face, not via the edges, and we believe this provides more representative diffusion data [69]. The tank is emptied periodically and coupons are removed for weighing. Fully immersed coupons can be placed in the tank for comparison. Temperature is controlled and measured continuously as for other aging tanks so that a temperature range can be provided. Figure 15b provides an example of results and a comparison with full immersion. This type of equipment can also be used to quantify the effectiveness of protective coatings.

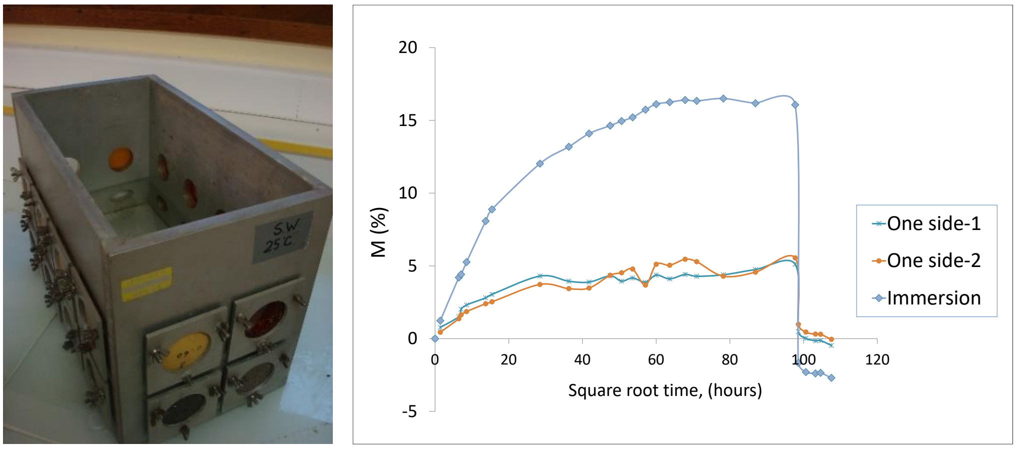


Figure 15. Uni-lateral water exposure tank. a) Equipment, b) Example of results for flax/acrylic composites, 12 months' immersion seawater 20°C, 3 months drying oven 40°C

A feature of natural fibres is their tendency to swell in water. This can be measured, and these data are necessary if water aging effects are to be modelled. Figure 16 below shows an example, for a flax reinforced acrylic and a glass reinforced epoxy. The dimensional changes are quite significant, and need to be considered during design.

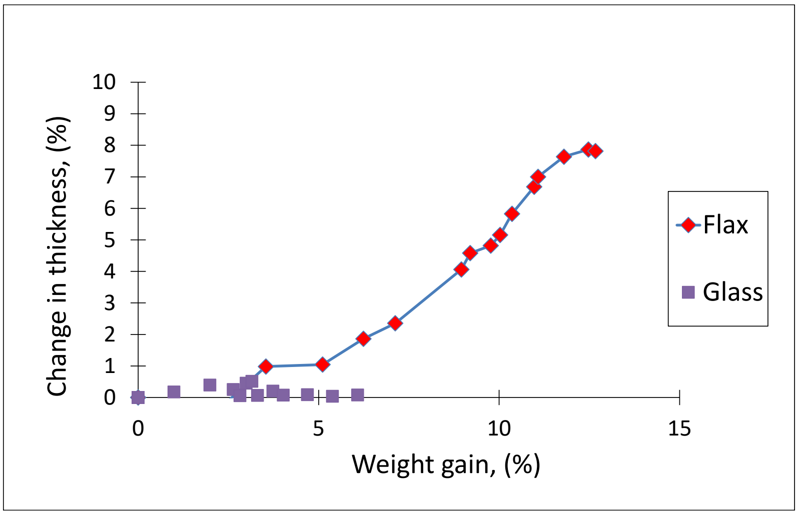


Figure 16. Measured through-thickness expansion during seawater immersion at 25°C of flax and glass fibre composites (4mm thickness, immersion time 5 weeks).

Another interesting feature of flax fibres, in contrast to glass or carbon, is a very non-linear tensile response, Figure 17. It is therefore essential to define the strain range when citing stiffness values, as the difference between initial and high strain stiffness can be considerable. In this example the tensile modulus varies from 14 GPa at strains up to 0.2% to 8 GPa at 0.5%. Several authors have examined this phenomenon, which is believed to be related to microstructural changes and elastic-visco plastic behaviour [70, 71, 72].

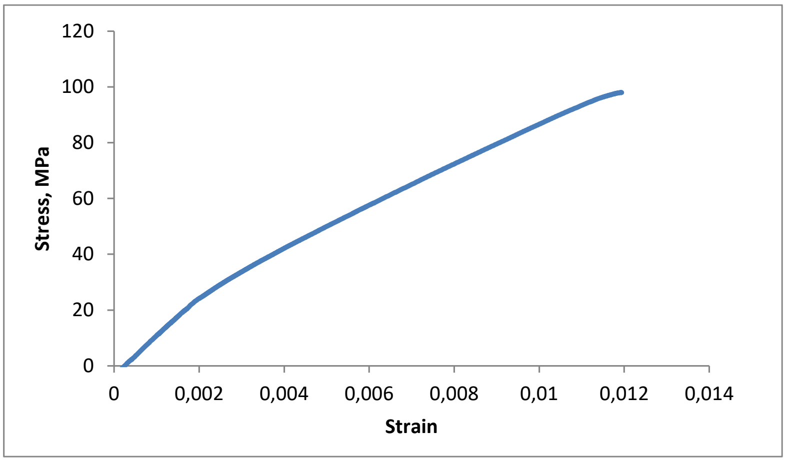


Figure 17. Tensile stress-strain plot, flax/epoxy composite

Another potentially interesting family of reinforcement fibres is cellulose. An example is rayon, once popular for tyre reinforcement, a fibre which is both bio-sourced and biodegradable. There has been some work on the use of these fibres to reinforce biobased resins and tensile strengths up to 300 MPa were measured [73]. These fibres are bio-sourced and biodegradable and of particular interest in applications with a high risk of loss at sea.

A third option being proposed as a lower impact reinforcement is volcanic fibres such as basalt. The latter shows very similar properties to glass, indeed both are high silica fibres. From a durability viewpoint they appear interchangable [74] though there is an additional 'corrosion' mechanism for basalt fibres under certain conditions [75]. Although these fibres are being promoted as a 'green' reinforcement the evidence for lower environmental impact compared to glass fibres is limited at the time of writing.

Alternative matrix polymers

As noted above, in the context of the need for more sustainable marine materials there is a tendency towards the use of thermoplastic matrix composites which can be recycled. These may be bio-sourced, such as PLA (poly(lactic acid)), or petro-sourced (PP, Polyamide). For semi-crystalline polymers such as PLA, PP or Polyamides the degree of crystallinity depends on the manufacturing route so any attempt to predict composite performance from matrix aging tests must verify this parameter. In general the water uptake is mainly in the amorphous part of the polymer so higher crystallinity, resulting from slow cooling after moulding for example, will lead to lower water uptake.

Another recent matrix development is the acrylic resin proposed by Arkema, mentioned in the Surface Vessel section above [16]. It is potentially attractive from an environmental viewpoint as after manufacture like a thermoset, by infusion for example, the cured matrix is thermoplastic. The monomer can be recovered after service and reused. The resistance after seawater immersion of composites based on this polymer, with glass and carbon fibre reinforcement, has been evaluated to be as good as that of a typical marine epoxy [17]. From a characterization viewpoint these polymers can be investigated in the same way as the traditional matrix materials

Concerns over the environmental impact of materials lost at sea, for oceanographic, military and fishing applications, is leading to more studies on marine biodegradable polymers such as the PHA family (poly(hydroxyalkonates)) [76] or PBS (poly(butylene succinate)) based polymers [77]. As these are sensitive to degradation by micro-organisms the use of natural seawater in aging studies can induce biodegradation. Accelerating water diffusion by increasing the temperature may not be appropriate for such polymers, as the micro-organisms which degrade them may not survive at higher temperatures. Beyond this difficulty there is a more general problem with biodegradability testing. The standard respirability tests are based on measuring CO_2 [78] or oxygen, but the test conditions may or may not be relevant to the degradation of polymers or composites on the seafloor. This is a complex, multi-disciplinary area of research, where input from biologists and micro-biologists is essential in order to understand and predict the degradation mechanisms.

Alternative sandwich cores

As noted above, sandwich core materials, particularly foams, are extensively used in the marine industry. The reference marine core material has been PVC (poly(vinyl chloride) for many years. It shows excellent mechanical behaviour and is available in a range of densities usually in the range from 45 to 200 kg/m^3 [79]. Natural cores such as balsa wood have also been used for many years [80]. However, there is environmental pressure to replace the PVC foams, and PET (poly(ethylene terephthalate)) foams are one of the candidates. These can be sourced from recycled PET bottles and are themselves recyclable thermoplastics [81, 82]. There have therefore been various studies on these foams, under both quasi-static and dynamic loads [83, 84] to compare them to existing materials. The characterization methods are similar to those for traditional sandwich materials and PET foams tend to show lower strengths at equivalent density. Nevertheless the advantages in terms of environmental impact are leading to more extensive use of these materials.

Concluding remarks

The initial premise that composite durability in a marine environment could be defined by a 'put it in water and see what happens' methodology has evolved significantly over the last 30 years. First, the application of more representative test conditions, circulating natural seawater under controlled temperatures, has removed some of the uncertainty in diffusion data. These tests were then modified to apply to natural fibre composites. And more recently, biological effects on composites have been included.

From a structural viewpoint, specific tests have been developed to simulate both the static and dynamic loads to which surface vessels and underwater structures are exposed.

Then, coupling between mechanical loads and water diffusion has been investigated; this remains an important suject today, particularly for highly loaded marine renewable energy structures.

Finally, the major challenge today is to reduce the environmental impact of the composite materials used at sea. Eco-design, based on Life Cycle Analysis, requires robust durability data to validate material choices. A nominally lower impact material may not satisfy environmental requirements if it has to be replaced more frequently. Durability testing will therefore remain an essential element of the energy transition.

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Data availability

Data sets generated during the current study are available from the corresponding author on reasonable request.

Competing interests

The author has no competing interests to declare that are relevant to the content of this article.

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