Towards More Representative Accelerated Aging of Marine Composites

Peter Davies

1 Introduction

The use of composite materials for critical structural applications at sea is increasing, particularly for energy recovery applications. The required lifetimes are typically from 5 to 25 years, but experience has shown that these may be extended further when end of life approaches. Civil engineering structures such as bridges and coastal infrastructure are designed for much longer lifetimes. The nature of many marine installations, in deep water for offshore oil & gas production, or in highly energetic ocean conditions for renewable marine energy, makes intervention and maintenance costly and dangerous. The end user requires guarantees that either the material properties will be maintained over these periods or the possible degradation is sufficiently well understood to allow quantitative estimation of property changes.

A major challenge for materials laboratories today is therefore to predict with confidence the long term durability of composite materials immersed in seawater and exposed to a range of mechanical loads. In many projects the time available to evaluate a material is short, a few months at best, so accelerated testing is unavoidable. This is not a new subject. Accelerated aging tests have been used in many previous composite studies e.g [1], and particularly for marine structures [2, 3], but it is attracting considerable interest today for a wide range of other applications. Recent examples include the wind turbine [4], civil engineering [5], aerospace [6] and automobile [7] industries. For all these applications there is a need to rapidly quantify the influence of degradation on long term performance. It is therefore essential to examine how this can be achieved and the limitations of the accelerating parameters.

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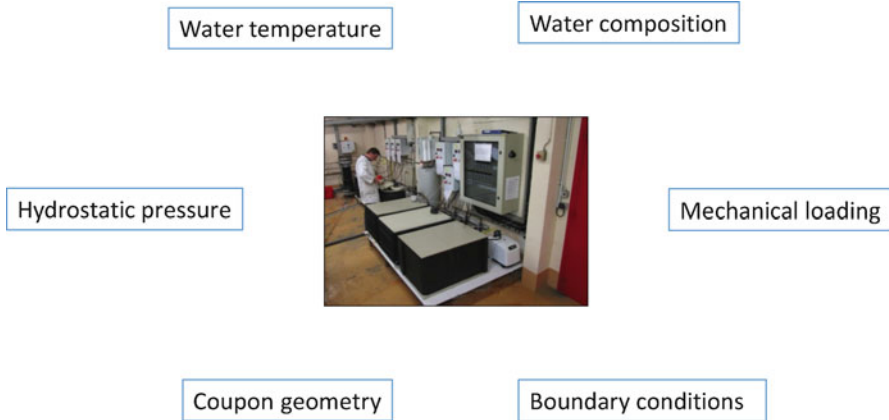Marine Structures Laboratory, IFREMER Centre Bretagne, Plouzané, France
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Fig. 1 Seawater aging test facility, showing heated renewed seawater tanks, with parameters affecting aging time

This chapter will first examine the various parameters that can be used to speed up material aging mechanisms, temperature, pressure, aging medium and sample thickness. There are few relevant standard test methods, so published data are based on a wide range of test conditions. Figure 1 shows the main parameters which can be used to reduce aging time. These will be considered in detail in the next section.

Most published work on long term aging is based on data generated over a few months, at most a year. This provides no opportunity to verify the extrapolations made to predict behavior after longer times. However, some samples have been aged in the laboratories at IFREMER for up to 8 years, at different temperatures, and data for these can help to validate (or not) the extrapolation of data from accelerated tests. Two examples will be discussed below, involving glass and carbon reinforced composites.

2 Acceleration by Increasing Temperature

The most widely applied approach to evaluate the influence of long-term exposure of a material to seawater is to increase the water temperature. This approach generally assumes an Arrhenius dependency of the properties of interest, namely the diffusion coefficients, so that by immersion at different temperatures the accelerating factors for water ingress can be determined experimentally [8]. Short immersion diffusion data at low temperature can thus be extended to longer times. This approach, potentially very powerful, poses a number of questions.

First, it must be verified that the Arrhenius approach actually applies to the material under the conditions of interest. Figure 2 shows an example of a set of epoxy resin weight gain plots for an immersion period of 400 days.
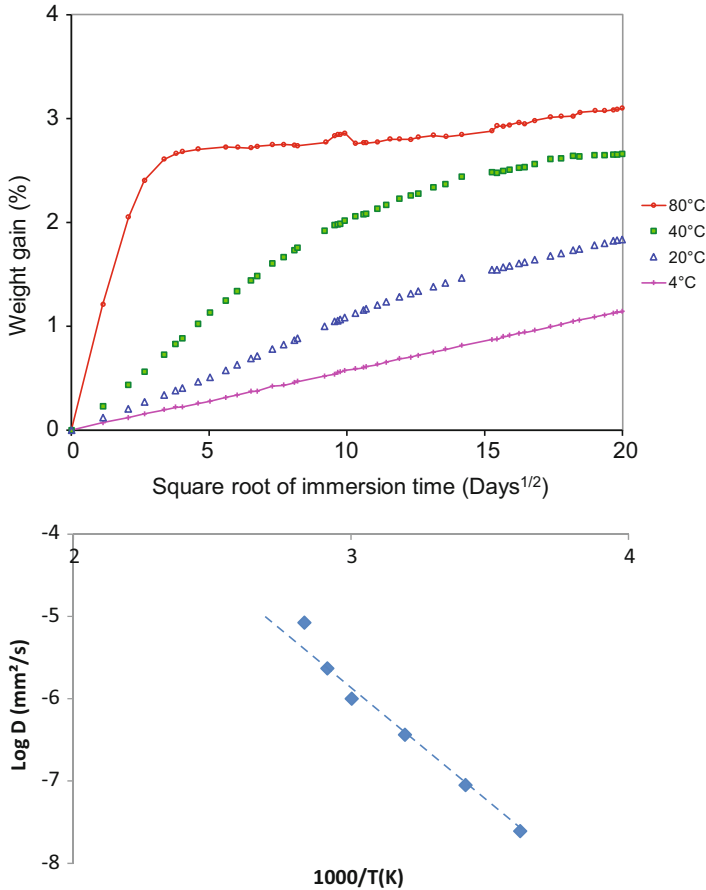
Fig. 2 Immersion of behavior of epoxy resin in sea water at different temperatures
Upper: Weight gain versus square root of immersion time, Lower: Arrhenius plot

Figure 2a shows that for 5 mm thick coupons of this amine cured epoxy resin, a grade widely used for wind turbine blade composites, a reasonably stable resin weight gain can be achieved in around 2 weeks at 80 °C, but it requires over a year at 40 °C to reach the same weight gain level. If it is assumed that the weight at saturation is the same at all temperatures (2.75% here) then diffusion coefficients at different temperatures (here 4, 20, 40, 60, 70 and 80 °C) can be estimated and plotted on an Arrhenius plot. A reasonably linear fit can be obtained up to 70 °C, then for the highest aging temperature (80 °C) the diffusion coefficient is higher than expected from extrapolation of aging at lower temperatures. Longer exposure at 80 °C also results in further weight increase above the plateau value. The dry Tg of this resin is around 80 °C, so this increase occurs at a temperature above Tg.

This example already shows that in order to affirm with any confidence that an Arrhenius approach can be applied it is preferable to perform tests at a large number of different temperatures. Celina and colleagues have discussed this point for rubbers

in [9]. There is no a priori reason that increasing temperature will not introduce additional diffusion mechanisms so this must be checked.

A second important question is by how much can the temperature be increased? The basic aim is to accelerate diffusion while not changing any other aspects of the material behavior. A prerequisite is therefore that the immersion temperature will not change the physical state of the material, by post-curing for example, so this must also be checked. A preliminary step in any accelerated aging study therefore involves physico-chemical analysis, DSC (differential scanning calorimetry) for example, before selecting the temperature to be used. This provides information on polymer transitions and in particular the glass transition temperature of the dry polymer, Tg. Once this has been identified, a common rule-of-thumb is to work at a maximum temperature of Tg-20 °C. However, this margin is based on the hypothesis that the Tg of most epoxy matrix resins will only drop by a few degrees after prolonged immersion and this may not be justified. Table 1 shows some examples of Tg values for epoxy matrix resins. A high temperature cured epoxy shows a drop in Tg after saturation of 36 °C, while a low temperature cured marine resin shows a drop of around 15 °C.

A more exhaustive study by Wright suggested an empirical relationship between weight gain and drop in Tg with a reduction in Tg of around 20 °C for each percent increase in moisture content [13]. For other materials, the sensitivity of the Tg to water may also be significant. Figure 3 shows the dramatic drop in Tg of polyamide

Table 1 Influence of moisture on Tg of matrix resins

Resin/hardener	Tg dry	Tg at saturation	Weight gain at saturation, %	Reference
Epoxy/Amine 1(HT cure)	170	134	2.5	[10]
Epoxy/Amine 2(LT cure)	75	60	2.8	[11]
Polyamide 6	66	−9	10	[12]

**Fig. 3** Influence of Tg of polyamide 6 on water content [12]
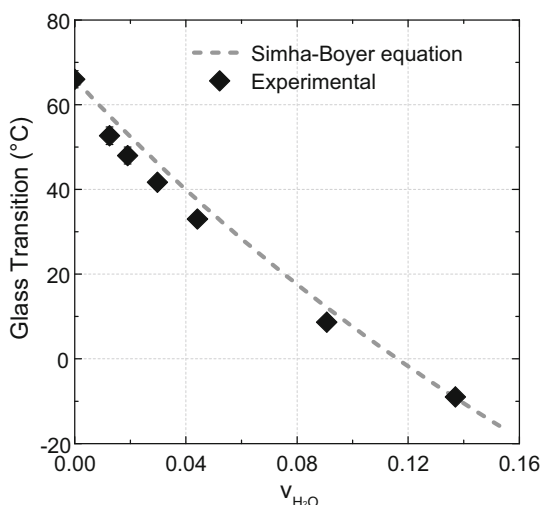
6 with water content, and it is clear that a test on this polymer which starts with the test temperature below Tg will become a test above Tg as the material state changes with time. This has been addressed in [12], where different diffusion models were needed to simulate diffusion behavior above and below Tg.

If the Arrhenius approach is valid and allows saturation of the material in a reduced time this can enable subsequent mechanical tests to be performed on specimens with a homogeneous water profile; this is the test protocol which many test laboratories use today to evaluate the durability of materials for marine applications. While this is certainly a useful first step, and allows a first material selection to be made, it gives no information on the lifetime of the material. The definition of end-of-life will depend on the application, but if resin molecular chain breakage (hydrolysis) is possible, which will cause a significant loss in mechanical performance, then tests must be sufficiently long either to provoke this mechanism or to show that it will not occur in the period of interest. This is discussed in more detail in Sect. 8 below.

3 Acceleration by Applied Mechanical Loads (Stress-Diffusion Coupling)

While temperature is widely used to accelerate diffusion, the previous section indicates that there are a number of potential difficulties. It is therefore tempting to examine whether other factors can be used, and in particular mechanical loading. The simplest approach is to apply a tensile stress to a specimen in water, but this requires a dedicated test bench, such as the one shown in Fig. 4. Early studies on epoxy resins by Fahmy and Hunt [14] in four point flexure indicated that tension increases the diffusion coefficient while compression reduces it. They explained this in terms of free volume changes but even at the highest stress level, the difference was only a few percent.
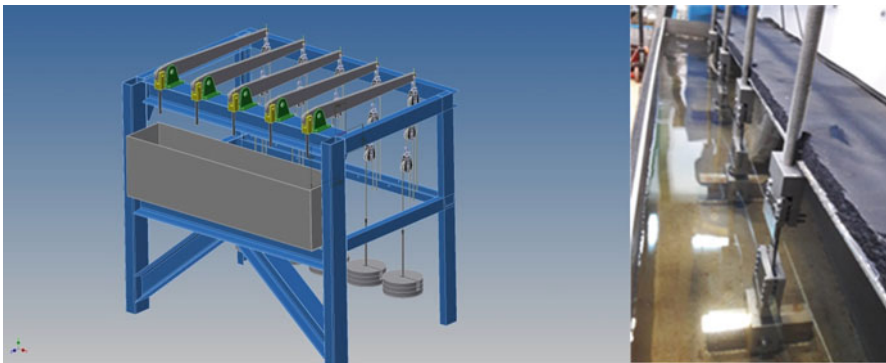
Fig. 4 Test set up to examine how applied tensile stress affects water ingress, and specimens in place
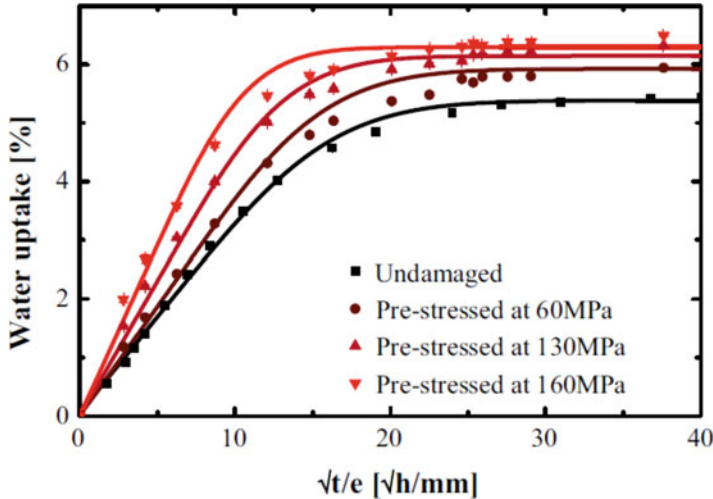
**Fig. 5** Influence of different tensile preload stresses on weight gain in water at 60 °C of ±45° specimen

To examine this effect for composites it is important to define load levels with respect to damage initiation. Low applied loads, which remain in the elastic response region of the polymer and below the damage threshold, will generally have a small influence on diffusion. Higher loads applied to composites will introduce damage, in particular resin cracking in off-axis plies, which can strongly affect water entry. Several authors have examined these effects [15–17].

A recent study has used the set-up shown in Fig. 4 to examine the influence of both pre-loading (applying a load before immersion but no load applied during aging in water), and loading during aging in water, on weight gain. Figure 5 shows that there is a small effect of preloading on weight increase. The matrix resin of a ± 45° specimen immersed in water will pick up about 5% by weight at saturation, and this may increase to around 6% if the specimen has been preloaded to a stress close to its break load [18], Fig. 5.

A more significant effect is noted when similar specimens are loaded in water at 60 °C, Fig. 6, In this case weight gain may reach 9% by weight and some specimens fail prematurely.

4 Acceleration by Increasing Hydrostatic Pressure

An alternative approach to accelerate the water ingress mechanically is to increase the hydrostatic pressure during immersion, in order to try to "push" the water into the material more quickly. Pressure increases with immersion depth, so data on pressure effects are also of direct interest for underwater applications of composites. Various authors have examined their influence [19–21].
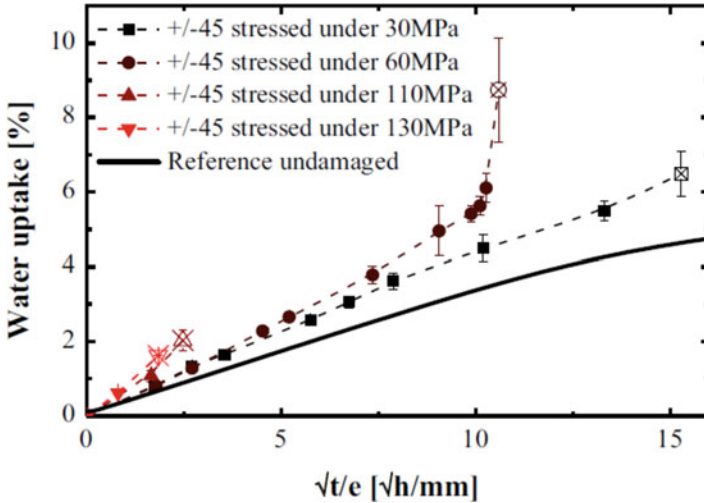
Fig. 6 Example of the influence of applied load on diffusion kinetics for ±45° specimen in water at 60 °C

Fig. 7 Pressure vessel to examine influence of pressure on weight gain. 100 MPa capacity vessels placed in temperature-controlled ovens, together with immersed reference coupons without pressure
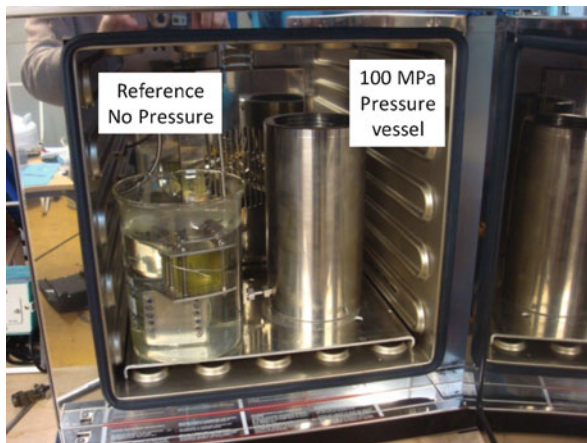
Two effects on water diffusion might be envisaged; the first, pressure to accelerate water entry, acts against the second, a polymer volume reduction due to pressure which will reduce available volume for water to fill. However, very high pressures are needed to produce significant volume reductions. Figure 7 shows test equipment developed to perform such tests.

This facility has been used to study a number of composites, some results have been published [22, 23]. While in one particular case, in the presence of high void content, a strong influence of pressure was noted; in all other cases the effect was quite small. Figure 8 shows two examples of results [23], for weight gain at pressures up to 50 MPa.
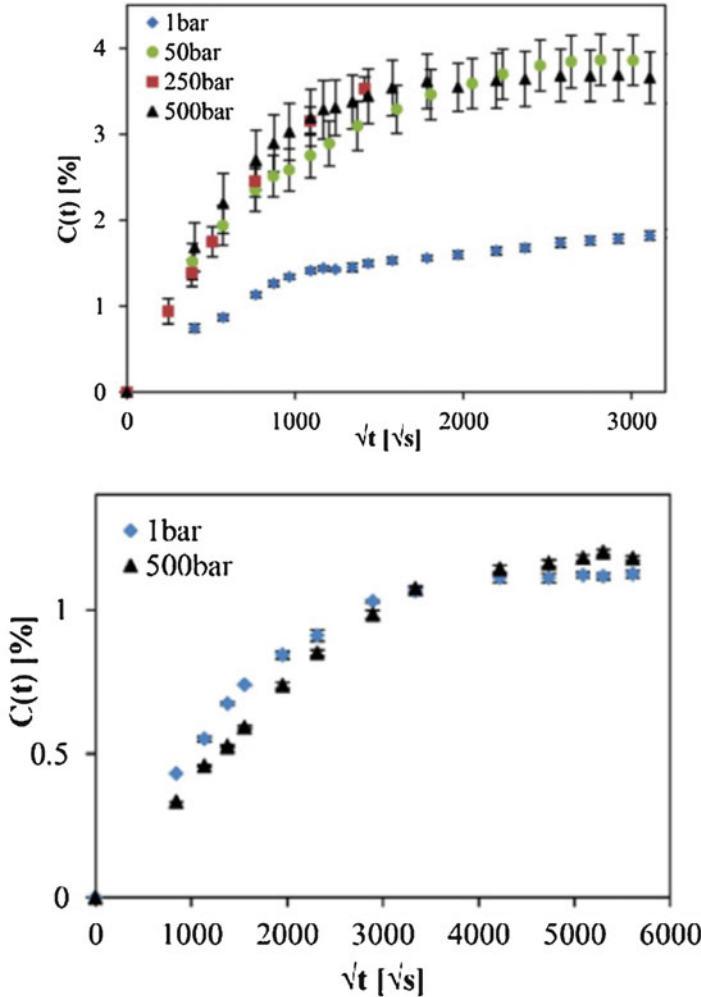
Fig. 8 Influence of hydrostatic pressure on weight gain for two glass/epoxy composites. Upper: Hand lay-up, Lower: Infused

These results indicate that it is unlikely that hydrostatic pressure can be very helpful in accelerating water entry into well-made composites.

5   Acceleration by Modifying Coupon Geometry

Another approach is to optimize the coupon geometry, and three modifications may help to saturate composites more quickly. The first, and most effective, is to reduce the material thickness. The formulation of Fick's law indicates that weight gain
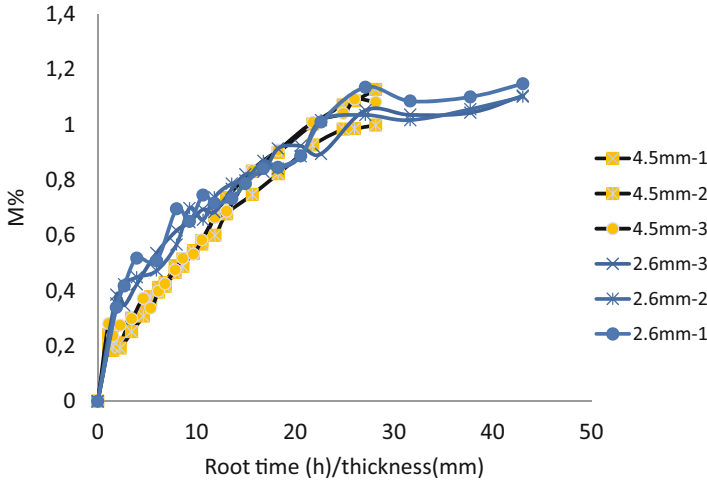
Fig. 9 Influence of coupon thickness on weight gain for carbon/epoxy composites, immersion 18 months in sea water at 40 °C. Three coupons for each thickness

depends in a linear manner on the inverse square root of sample thickness. Thus if the material is indeed Fickian it should be possible to reach saturation in a quarter of the time by halving sample thickness. Wang et al. suggested a similar approach recently for epoxy resin [24]. This is an attractive way to reduce aging time, although for composites there is a practical limit to the extent to which thickness can be reduced without changing the material microstructure. Thin composites tend to have higher fibre volume fractions than thicker materials, and thermal conditions during cure may vary with thickness. The strong relationships between manufacturing, structure and properties in composite materials must also be considered.

Figure 9 shows weight gain plots for quasi-unidirectional carbon/epoxy coupons of 2.6 and 4.5 mm thicknesses, produced by infusion, immersed in seawater at 40 °C. When the data are normalized with respect to coupon thickness the curves superpose quite closely.

A second possibility is to reduce the size of the coupon, encouraging water to enter through the specimen edges. Early work by Springer and colleagues discussed the influence of specimen geometry on diffusion measurements, and a simple expression was proposed for edge effects for isotropic materials [23]:

$$D = D_x \left(1 + \frac{h}{l} + \frac{h}{w} \right) 2 \tag{1}$$

where D is the measured value from the initial slope of the weight gain versus square root of time plot, D_x is the through-thickness diffusion coefficient, h is the coupon thickness and l and w are the length and width. It should be noted that these corrections are not negligible; for a 50 mm × 50 mm coupon they indicate an over-estimation of D_x by 8% for a 1 mm thick resin sample and by 25% for 3 mm.
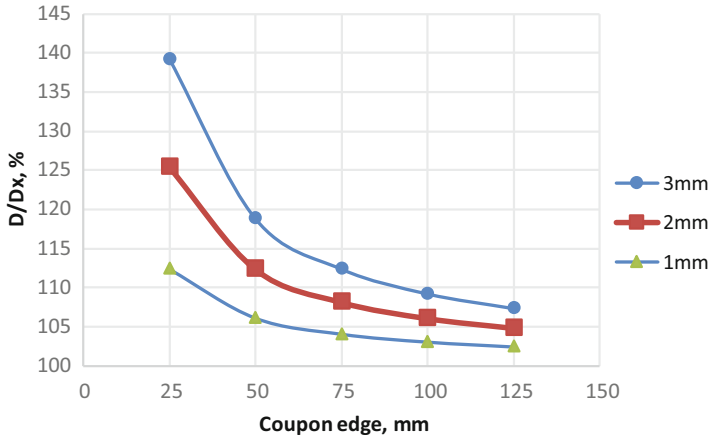
Fig. 10 Effect of square coupon size on water ingress rate for different coupon thicknesses, taking $D_y = 4 D_x$ and $D_z = D_x$ from [26]

Reducing coupon size may still be helpful to reach saturation of a thick resin sample more quickly, but for fiber reinforced composites the situation is more complex, as diffusion is anisotropic, with a preferred orientation along the fiber direction. The expression proposed for diffusion into composites in [25] is:

$$D = D_x \left(1 + \frac{h}{l} \sqrt{\frac{D_y}{D_x}} + \frac{h}{w} \sqrt{\frac{D_z}{D_x}} \right) 2 \qquad (2)$$

Ratios between in-plane (y-z) and through thickness (x) diffusion coefficients can vary considerably, but in order to illustrate how coupon size can affect the D/D_x ratio and lead to overestimations of through-thickness diffusion coefficients the values given for a glass/epoxy composite in [26] will be used here. Figure 10 shows some examples of the influence of coupon dimensions.

A third possibility to accelerate water ingress is to adjust the fiber orientation. This has been discussed above, and various authors have used the fact that diffusion in the fiber direction is faster than in the other directions to characterize the different coefficients [27, 28]. Based on this difference in certain cases, for example when unidirectional composites are being studied, it may be possible to choose a coupon geometry which increases water access along the fiber direction in order to saturate them more quickly. A rectangular coupon cut with its longer dimension perpendicular to the fiber direction would be expected to saturate more quickly than one with the same surface area but a standard square geometry. However, the possibilities for using such an approach to accelerate aging are quite limited, particularly if the aim is to measure residual properties after aging rather than diffusion kinetics; geometries are then defined by standard test methods.

6 Influence of Aging Medium on Acceleration

For marine applications, the environment of interest is natural seawater. However, many aging tests are performed in either tap water or distilled water, more readily available in most laboratories than natural seawater. The former have a higher chemical activity than seawater, so it might be possible to use this difference to accelerate water ingress. Figure 11 shows an example of results from a 2 year immersion test performed at 40 °C on the same pre-preg glass/epoxy composite in deionized water and natural seawater. The initial parts of the plots are quite similar, but there is clearly a faster weight gain in deionized water later. After 2 years, the samples in seawater have reached a weight gain similar to that which those in deionized water had reached after only 1 year. However, as neither have achieved a stable weight it is not possible to conclude on whether they would reach the same final weight gain. Results for an infused glass/epoxy composite indicated slightly lower saturation values in seawater.

Various authors have discussed the influence of specific interactions between polymers and water on diffusion, and these can explain many of the anomalies noted for diffusion plots. Colin has discussed these recently [29], and showed that it is interactions between water molecules and polar groups in the polymer matrix, rather than free volume, which determine the amount of water which enters a polymer. There is a good correlation between solubility parameters and mass at saturation for a range of polymers including different epoxy/amine networks. However, the relationship between polymer structure and diffusivity is less clear. Merdas et al. [30] have found that diffusion rate is slowed down by molecular interactions in amine cured epoxies.
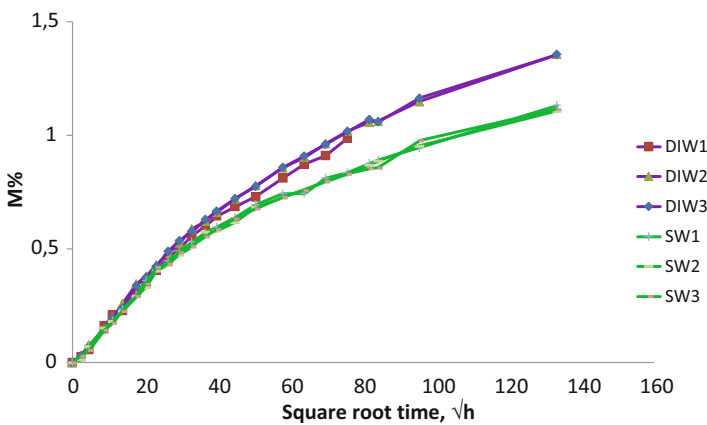
Fig. 11 Influence of immersion medium on weight gain for two composites, 3 coupons for each medium

Table 2 Examples of accelerating factors for weight gain, with respect to an immersion in seawater at 25 °C without mechanical loading, thermoset matrix composites

Temperature: 40 °C	Temperature: 60 °C	Applied strain: <0.2%	Hydrostatic pressure: 50 MPa	Medium: Deionized water	Thickness: reduced by 50%
×3.5	×10	×1.5	×1	×2	×4

7 Summary of Acceleration Factors

Table 2 shows a very simplified summary of the preceding sections, providing orders of magnitude of the acceleration in weight gain that can be achieved. Order of magnitude values are shown, to give an estimate of how the time to reach a given weight gain can be reduced. This clearly shows that the two parameters likely to be most effective in shortening test time are raising temperature and reducing coupon thickness. The other parameters may be of interest for specific applications such as deep sea structures, but their benefits in terms of aging acceleration are likely to be minor.

This table also shows the limits of accelerated aging strategies. Even under the most favorable conditions, and taking into account all the risks described above, it is unlikely that an accelerated aging campaign lasting less than a year will be able to provide useful information on the long term behavior of composites.

8 Examples of Long Duration (> 5 Year) Immersion Studies

The duration of the majority of published studies on wet aging is less than 1 year. A few longer studies have been reported. For example, Kootsookos & Mouritz describe a study of polyester and vinylester composites immersed in seawater at 30 °C for over 2 years [31], but this is unusual.

In this section, two examples of much longer immersions will be presented, in order to discuss the validity of predictions of weight gain after accelerated aging, by comparing with long duration ambient temperature measurements.

8.1 Carbon Fiber Reinforced Composite

In this first example, carbon fiber reinforced composite specimens were immersed in natural seawater for 6 years. The interesting point here is that not only three aging temperatures were used (25, 40 and 60 °C) but also that different coupon thicknesses were investigated. This has allowed both of the most promising accelerating strategies discussed above to be studied. Table 3 describes the materials studied. Fiber volume fractions were estimated to be in the range 59–61%.

Table 3 Carbon/epoxy samples for long term aging study

Fiber	Matrix	Cure cycle	Tg dry °C	Density	Thickness, mm	Orientation
T700	SR1710 epoxy, amine hardener	10 h 60 °C	79	1.556	2.5	4x quasi-UD
			80	1.545	4.5	7x quasi-UD
			82	1.537	11	18x Quadriaxial
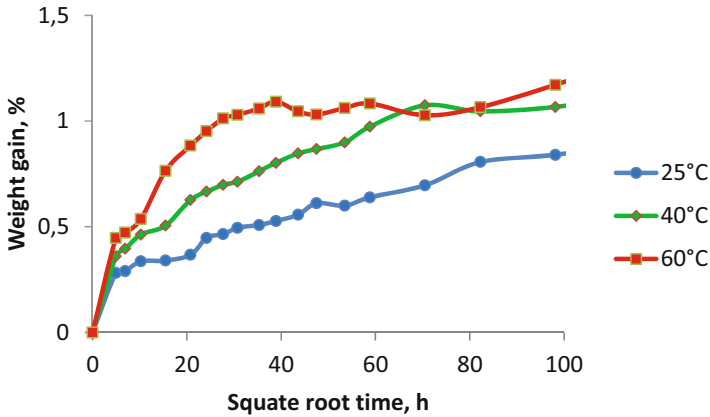
Fig. 12 Weight gain plots, carbon/epoxy, 2.5 mm thick coupons, 1 year immersion natural seawater. Each point corresponds to the mean of measurements from three samples

Figure 12 shows examples of the basic initial weight gain plots, for 2.5 mm thick coupons at each temperature.

These clearly show the accelerating effect of temperature. The 60 °C reached a reasonably stable weight gain around 1% after 2 months, the 40 °C sample takes around 7 months to get to a similar value, and after 1 year in seawater at 25 °C the weight gain is lower, around 0.85%. These are quite "well-behaved" materials, despite an initially high weight gain just after immersion. The samples were dried before immersion.

Longer immersion times, up to 6 years, revealed additional information. Figure 13 shows weight gain measurements for specimens of three thicknesses immersed at 60 °C. A plot for a coupon at 40 °C is also shown for comparison.

First, these plots show the influence of specimen thickness, with the time to saturation of the thinnest coupons being significantly shorter than for the thicker specimens. As an example, the approximate times to reach 1% weight gain are shown in Table 4 below. By reducing the thickness to about 25% (from10.5 to 2.5 mm) the time to reach 1% weight has been reduced from two and a half years to 1 month.
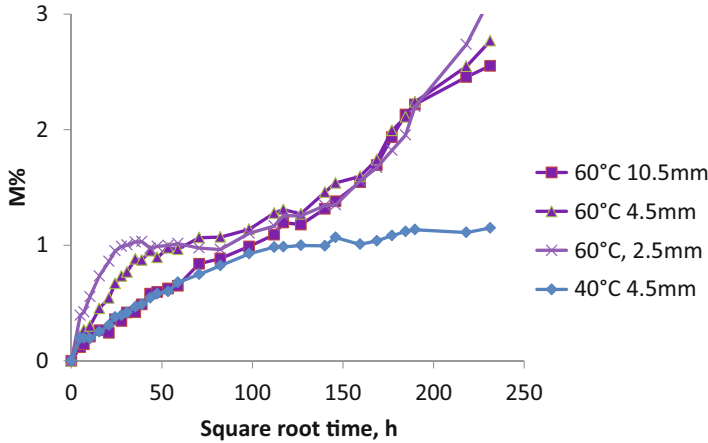
Fig. 13 Weight gain plots, carbon/epoxy, 6 years' immersion 60 °C, three coupon thicknesses

**Table 4** Time to reach 1% weight gain, 60 °C immersion

Thickness, mm	Time, days
2.5	32
4.5	144
10.5	886

The plots in Fig. 13 also reveal an increase in weight gain for coupons immersed at 60 °C, which starts after the same immersion time, around 1 year, for all three thicknesses. This suggests that it may be related to a surface degradation mechanism rather than volume degradation, and indeed a surface color change was noted. The increase in weight gain may be caused by the conversion of epoxies to more polar groups; chain scission would be expected to result in a mass loss rather than an increase. At the lower temperature, 40 °C, even after 6 years in water there is no indication of a weight gain increase for any of the coupons tested, but this may simply indicate a strong temperature dependency of this mechanism.

It may be tempting to use these plots to try to estimate the lifetime of these composites. The diffusion kinetics can be used to determine the time necessary to saturate a composite of any thickness, while a criterion based on the time to reach a weight gain increase at 60 °C (about 1 year) might be employed to extrapolate to the time required for the material to start to degrade at a lower temperature. There is no evidence of change after 6 years at 40 °C, and given the accelerating effect of at least 4 in raising the temperature from service immersion conditions, typically 15–20 °C, to 40 °C the lifetime of this composite should exceed 20 years. This provides a very conservative first criterion for lifetime. Clearly in order to examine how the properties of interest change once the resin starts to degrade requires mechanical testing, as the fibers can continue to support loads beyond this first damage initiation. In this study short beam shear tests were performed. Figure 14 shows results for ILSS (interlaminar shear strength) measured on wet 4.5 mm thick specimens after different immersion periods.
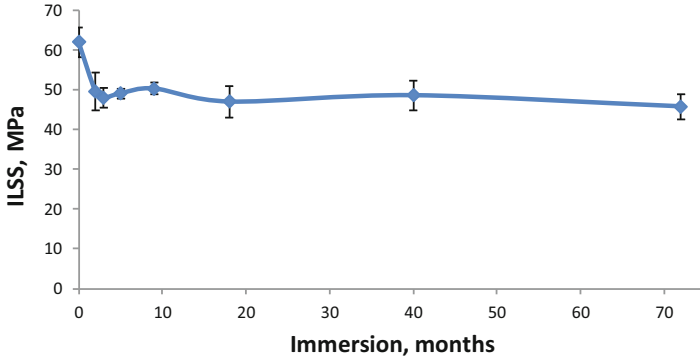
Fig. 14 ILSS values versus immersion time in seawater at 60 °C, carbon/epoxy
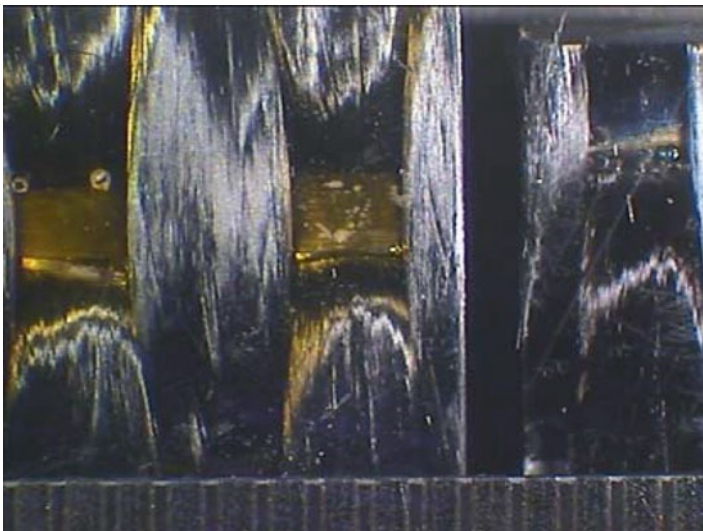
Fig. 15 ILSS specimen surfaces
Left: 6 years 60 °C. Right: 6 years 25 °C. Millimeter scale

There is an initial drop in strength that occurs quite quickly, within 2 months, which may be caused by plasticization. However, then the strength remains remarkably constant even after 6 years in seawater at 60 °C. This appears to confirm that the weight gain increase noted at 60 °C is probably a surface effect, and does not affect through-thickness properties significantly. Observation of the specimen surfaces revealed a yellowing of the matrix resin, Fig. 15. Despite the changes on the weight gain plots the ILSS values are still high after 6 years.

8.2 Glass Fiber Reinforced Composite

Another long duration aging study was performed on glass/epoxy laminates, lasting nearly 8 years. The material is described in Table 5, and some data from this project have been presented previously [32, 33]. The epoxy resin is a DGEBA based system that has been widely used for filament winding and it is still being used today. The hardener employed in this study was an anhydride, and it is (now) well known that these are susceptible to hydrolysis if exposed to water at elevated temperatures [34, 35]. In the application here the material was to be used in cooling water pipework exposed to temperatures up to 60 °C, so the initial aim was not to accelerate tests but rather to examine the material response at service temperatures; however, a set of samples was aged in tap water at different temperatures, (25, 40 and 60 °C), and it is this database which is of interest here.

Figure 16 shows examples of weight gain plots for this material in distilled water at three immersion temperatures. At 20 °C the diffusion plot stabilized at a weight gain of around 0.5%, and then a small increase was noted after about 7 years. At 40 °C the weight gain exceeded this value after around 2.3 years, while at 60 °C weight gain increased beyond this value after only 1 year. At the highest temperature weight gain increased to over 3%, and then fell to below the initial sample weight (not shown on Fig. 16).

Table 5 Glass/epoxy samples for long term aging study

Fiber	Matrix	Cure temperature	Tg dry	V_f	Thickness, mm	Orientation
E-glass	LY556/HY917	140 °C	115 °C	53%	3	$\pm 55°$
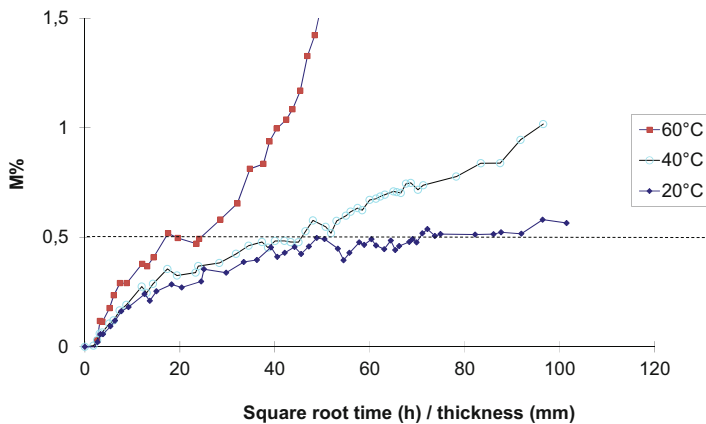
Fig. 16 Examples of weight gain plots, glass/epoxy, immersion in distilled water for 7.7 years

Table 6 Mechanical tests performed wet after 3 years in distilled water at 60 °C

Panel	Flexural strength, MPa		ILSS, MPa	
	35°	55°	35°	55°
Unaged	410	127	44	20
60 °C 1%	302	120	43	19
60 °C 3%	231	87	30	13

Fig. 17 Weight gain panel (200 × 300 mm^2) after 7.7 years in distilled water at 60 °C, and unaged reference strip

These results underline the risk of raising temperature to accelerate water ingress into this composite formulation. At 60 °C the matrix resin undergoes hydrolysis with chain scission and reduction in cross-link density.

The coupons used for weight gain measurements were large, 200 × 300 mm^2, and after 3 years two of the five immersed at 60 °C were used for mechanical tests. Three point flexure and short beam shear tests were performed in both directions of the panels. Table 6 shows results. The two panels immersed at 60 °C showed different weight gains after 3 years, 1% and 3%. Specimens from the latter had significantly lower strengths.

Figure 17 shows one of the panels used for weight gain measurements at 60 °C, together with an unaged reference strip. In this case the change in color is observed throughout the composite thickness, in contrast to the carbon/epoxy of the previous section for which it was limited to a very thin surface layer.

If aging tests are only performed for a few months, as is often the case, this hydrolysis mechanism will not be detected, even though it will probably be the limiting factor in long term use of the composite.

9 Other Factors Required to Improve Representativity of Testing

The results from many composite studies show large drops in mechanical properties of composites after quite short accelerated aging times under severe conditions. This creates a quite false impression of composites as materials that are sensitive to water. Interpretation of data from accelerated aging tests must relate sample geometry and test conditions to the form and environment of the structural component, and requires considerable care. The following factors should be considered:

- Many marine composite structures are very thick, and will never saturate with water in service. A difficulty in accelerated testing is to ensure that the accelerating factor (e.g. temperature) does not affect the homogeneity of degradation. For example if temperature is raised the laboratory degradation may be diffusion controlled, mainly affecting surface layers, whereas in service at lower temperatures it may be homogeneous [8]. This will depend on the characteristic times for diffusion and hydrolysis and the relative thicknesses of coupons and structures.
- It is very rare for a composite structure to be immersed at sea without a protective coating. This may be a gel-coat, an anti-fouling paint, or a specific water barrier layer. These will all slow water entry.
- There are few free edges in components, and those that exist will normally be protected, so diffusion times will only depend on the through-thickness diffusion coefficient.
- In many cases, boat hulls for example, water only has access to one composite surface.
- Immersion is often discontinuous, allowing regular drying periods.

The length of this list highlights the limitations of current test practice. Some of these points can be accounted for by modelling. For example, once a diffusion model has been validated by testing thin coupons it can, in theory, be included in a numerical model to allow the water profile through any thicker section to be determined. An example for a 20 mm thick tidal turbine blade can be found in [36]. The model results showed that only 8% of the thickness of the blade would be saturated after 25 years in seawater at 20 °C.

There are very few studies which quantify the influence of coatings on the long term behavior of composite marine structures. This may be justified by assuming a worst case scenario, where the coating is an extra benefit but which may be eroded or otherwise removed during service. Nevertheless, it can significantly reduce water ingress and a realistic lifetime model should include it. Again, if the diffusion properties of the coating are known it can be included in a numerical analysis.

The fact that composite structures are rarely fully immersed suggests that a more representative test would apply water to only one surface of a specimen. Equipment has been developed for uni-facial testing to study coating performance and in particular the kinetics of blistering due to osmosis [37, 38], Fig. 18. It is simply a water-filled, temperature controlled test tank with circular openings, onto which the

Fig. 18 Aging tank for uni-facial exposure of composites to water, without edge effects

samples are clamped. The inner surface of the sample is exposed to water; the outside will be exposed to laboratory temperature and humidity conditions.

This can be applied to study water diffusion kinetics under more realistic conditions, also avoiding coupon edge effects.

Finally, equipment such as oceanographic measurement devices or seismic equipment is immersed during service then stored between campaigns. If drying kinetics are known then they can be used to estimate the effect of drying periods on water profiles. The kinetics of drying may be different from immersion [39] and need to be measured. Again, numerical modelling can allow integration of these data to provide the response to in-service conditions. However, immersion/drying cycles may be more severe than continuous immersion and this is another area requiring more study. Drying cycles also provide valuable information on the reversibility of aging, and are strongly recommended.

10 Conclusions

This paper describes accelerated immersion tests of composites for marine applications. First, the various factors which can be used to reduce test time are discussed. It is shown that reducing sample thickness offers some advantages over the more usual approach of increasing water temperature. Then two examples of long term testing are presented, 6 years' immersion for a carbon/epoxy and 8 years' immersion of a glass/epoxy. These examples show the potential for accelerated evaluation of durability but also the limitations. Finally, a number of factors which need to be included to make test strategies more realistic are discussed.

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