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Influence of seawater immersion on acrylic adhesive properties and bond strength on wet composites

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Abstract :

This paper describes a study on an acrylic based adhesive developed for marine repair applications. The adhesive alone was aged for over 12 months and tensile samples were tested periodically to characterize the influence of seawater aging at 40 °C. The adhesive alone plasticizes in seawater, losing around 40 % of both modulus and strength after 12 months, but these are largely recovered after drying. In parallel, adhesively bonded glass and carbon fibre composite assemblies were tested after similar aging times. Both retain over 80 % of unaged apparent shear strength after 12 months in natural seawater at 40 °C. Adhesive bonding of wet composite substrates, which had been immersed in seawater for up to 12 months before bonding, was also evaluated to determine residual bond strength. The break strengths of assemblies of wet glass fibre composites were not affected by substrate immersion for up to 12 months before bonding, while strengths of carbon fibre composite assemblies dropped to around 50 % after prolonged substrate immersion. Reasons for this difference are discussed. The results suggest that this adhesive shows good durability and should be considered for marine repair applications.

Keywords : Adhesive, Seawater, Composite, Wet bonding

Introduction

Adhesive bonding of fibre reinforced polymer composites has long been recognized as an attractive bonding method, compared to the mechanical assembly alternatives such as riveting often favoured between metallic parts. Many authors have studied this topic and exellent textbooks are available [1-3] which describe design, surface treatments, testing and available adhesives. Adhesives are widely used in boat assembly and repair [4], the most frequent formulations being based on epoxies and polyurethanes. These allow a wide range of mechanical behaviours to be achieved, from rigid to very flexible. A third option is acrylics, which offer fast cure at room temperature, good fracture resistance and high strength [5-8]. They have been available for over 30 years but new grades are being developed for specific applications. One of these developments is a two component acrylic adhesive for 'fast repairs under tough conditions' [9]. This sounds attractive for marine applications, but there are a number of specific questions which must be addressed:

- How do the adhesive properties change with immersion time ?
- How does seawater immersion affect bonded composite assembly properties ?
- Can the adhesive be used to bond composites which have been previously immersed ?

The first two questions are crucial for evaluation of the lifetime of the assembly. The third one determines the extent to which the adhesive is appropriate for marine repair work.

All polymers are affected by water to some extent [10]. Previous studies on wet aging have mainly focused on epoxy formulations. For example, Rudawska looked at aging of epoxy samples in water with different salt concentrations at room temperature for up to 3 months. She found no significant change in strengths [11]. Gao et al examined epoxy-bonded aluminium in salt water [12] and showed that sodium and chlorine ions in salt water could accelerate degradation compared to tap water. Other aging studies on epoxy bonded assemblies have included water diffusion studies [13,14] and modelling to account for water aging effects [15-18].

There are far fewer results from investigations of aging of acrylic adhesives. Lyons et al studied the aging of acrylic adhesives, but focused on the influence of storage for up to one year on curing [19]. Avendano et al [20] and Hayashi et al [21] studied the influence of temperature, while Del Real et al examined the durability of acrylic bonded aluminium [22]. The latter showed that exposure to high humidity was more severe than immersion in deionized water or saline solution. Hou and Lu used residual shear strengths measured after high temperature exposure to water (80°C) to estimate aged acrylic adhesive shear strengths at room temperature [23]. Bordes et al investigated marine aging (immersion in salt water at three temperatures ; 20, 40 and 60°C) of acrylic adhesive (MA832 from ITW Plexus) and adhesively bonded steel double lap shear (DLS) specimens [24]. They plotted the

mechanical test results versus weight gain. For the adhesive initial dry modulus was 1.4 GPa and yield strength 25 MPa. These dropped to 0.8 GPa and 16 MPa after around 2% weight gain due to water uptake, when Tg stabilized, but values did not evolve further even after 8% weight gain. Values after aging at all 3 temperatures in sea and deionized water fell on the same curves. For DLS specimens aged at 20°C unaged failure stresses were around 14 MPa and dropped faster for seawater (to 8 MPa after 6 months) than in deionized water (still at 11 MPa after 12 months). Steel substrate corrosion was the reason for this difference, but the results suggested that the durability of acrylic adhesives might be interesting for marine applications. Aging studies on composite substrates assembled with acrylic adhesives are not common. Borsellino et al studied temperature effects on glass reinforced composite profile assemblies for civil engineering [25]. They compared epoxy adhesives to acrylics. The latter showed lower loads at failure but higher strains, for temperatures up to 90°C. It is also interesting to note that a range of acrylic based matrix resins for infusion of fibre reinforced composites has been commercialized recently under the trade name Elium™, from Arkema. A study on the seawater aging of these resins showed that they were at least as resistant to aging as traditional marine epoxy matrix resins [26]. Adhesives are widely used for repair. This is a subject which has received considerable attention, in particular for aircraft applications [27]. Many parameters influence bond strength (chemistry, surface preparation, curing conditions) and the Taguchi method has been applied to optimize bond strength [28]. Underwater repair applications have focused on steel pipelines and a number of polymer-based solutions exist. These include hoop winding of impregnated fibres and bonding of composite patch products [29-32]. There has also been considerable recent activity in the area of bio-inspired adhesives for underwater applications [33]. Repair to composite boat structures, and other marine infrastructure damaged in service [34] often also requires bonding to wet substrates, and the work described here was performed to evaluate adhesives in that context.

In conclusion, a brief review of existing literature provides many examples of durability studies on joints bonded with different epoxy adhesives. As for epoxies, acrylic adhesives englobe a large range of suppliers and formulations, but have received rather less attention to date. The particular acrylic grade studied here, recently commercialized and specifically designed for marine repair applications, has so far not been investigated in detail. The potential for bonding directly onto wet composite substrates is a major advantage for both field repair and laboratory studies, and the aim of the present work is to evaluate this possibility.

Materials and Methods

- Adhesive sample preparation

All test samples were manufactured at Ifremer in Brest. Araldite™ 2051 two-component acrylic adhesive panels 1.5mm thick were cast between two steel plates. 50 x 50mm² coupons were extracted for weight measurements, dumbell specimens (ISO 37 type 3 [35]) were machined using a Charly Robot™ milling machine. They are 50mm overall length with a central width of 4mm. All adhesives were cured at room temperature (20°C), no post-cure was applied here as these are often difficult to apply during field repair. Samples were left at least 48 hours after manufacture before testing or immersion.

- Composite substrate manufacture

Two composite substrates were produced, both with stitched quasi-unidirectional reinforcements, by resin infusion. Details of all the materials tested are given in Table 1. The reinforcements both contained a small amount of 90° textile stitching. The matrix resins are not identical but both are marine epoxies developed for infusion with amine-based hardeners.

	Fibre/resin	T_g, thickness, V_f
Bulk adhesive	Araldite™ 2051	71°C, 1.5mm
Glass composite substrate	Stitched E glass / Hexion RIM135-H137	77°C, 3.8 mm, 56%
Carbon composite substrate	Stitched T700i / Sicomin SR8100-SD4772	78°C, 2.2 mm, 65%

Table 1. Bulk adhesive and composite substrate characteristics

- Tg measurements

Glass transition temperatures, Tg, were measured before and after aging by Differential Scanning Calorimetry (DSC), using TA DSC25 equipment

The values given below correspond to the enthalpy slope change versus temperature for the first ramp at a heating rate of 10°C/minute. This heating rate is slower than the value suggested in the ISO standard (20°C/minute, [36]) but provides higher resolution. Values of Tg of unaged materials are shown in Table 1.

- Composite specimen preparation

Composite substrates were cut to dimensions of 100 x 25 mm². Some were bonded directly, to produce single lap shear (SLS) specimens for aging tests, others were placed in water to age them for different periods before bonding, in order to study the assembly of wet substrates. Figure 1 shows an overview of the experimental programme.

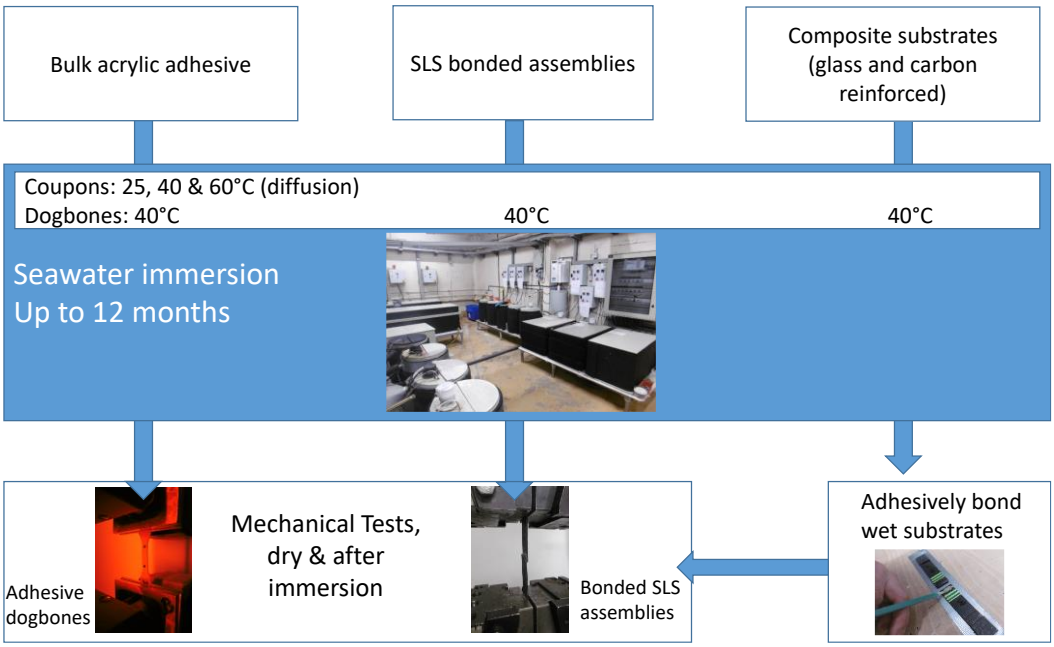


Figure 1. Overview of the experimental programme.

Figure 2 shows the lap shear specimen dimensions for all tests, substrate thicknesses given in Table 1.

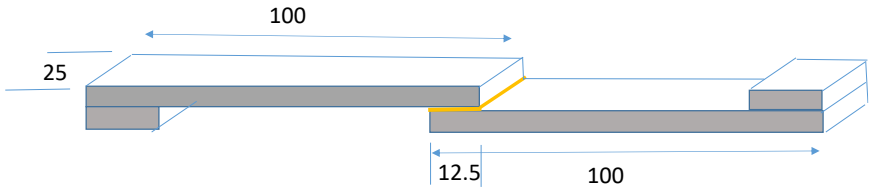


Figure 2. Single lap shear (SLS) specimen geometry (dimensions in mm).

The surface preparation for all dry specimens was abrasion with 180 grade paper followed by an alcohol wipe. Adhesive was placed on both surfaces with a pistol, they were then clamped individually. Bondline thicknesses were measured from polished images of specimen edges to be in the range 0.1 to 0.2mm. Two examples of images are shown in Figure 3.

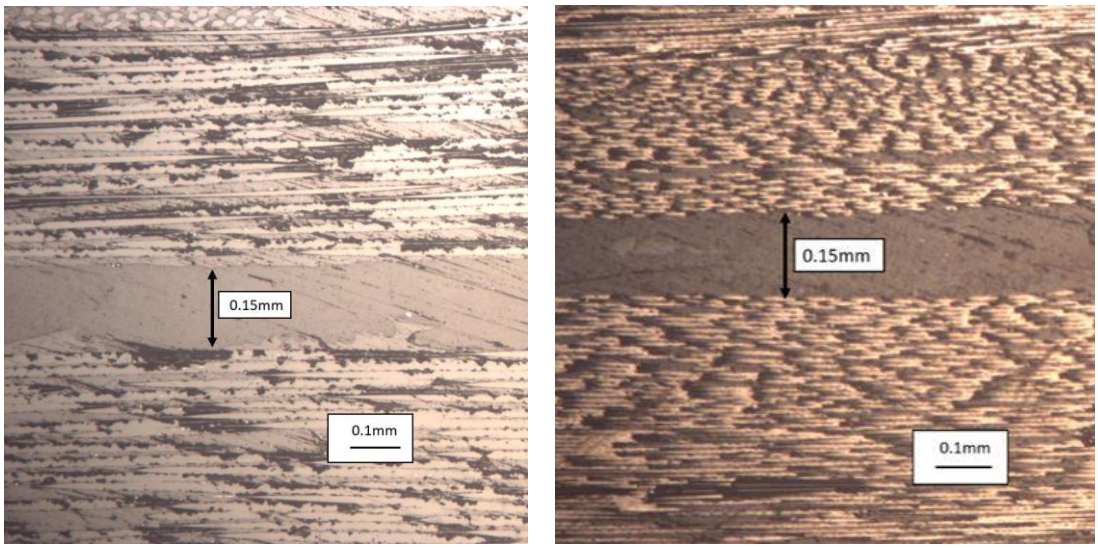


Figure 3. SLS bondline thickness measurements on specimen edges, left : glass, right: carbon.

Square (25x25mm²) blocks of the same composite material were bonded to the specimen ends (Figure 2) in order to align the specimen in the machine jaws before testing. The procedure for bonding wet substrates was similar to the one used for dry assemblies except that a 120 grade abrasion paper was used to prepare the surfaces. The surface was then re-wetted with seawater before applying the adhesive, the edges were cleaned with a spatula and the substrates were clamped together. The bonded specimens were then replaced in seawater for 24 hours at 40°C before testing.

- Mechanical testing

All mechanical tests were performed in a temperature and humidity controlled laboratory (21°C ±2°C, 50%RH ±5%). Bulk adhesive dumbell specimens were tested in tension on an Instron 5966 test machine with a 10 kN load cell, loading rate was 2 mm/minute. A non-contact Instron™ video 2563 provided strain values in the central parallel section. The SLS samples were assembled according to the geometry of ASTM D1002 with a 12.5 mm overlap. Lap shear tests were performed on the same Instron™ 5966 test machine, loading rate was again 2 mm/minute. Three to five samples were tested for each condition.

- Seawater aging conditions

Diffusion kinetics were examined by immersion of coupons in natural seawater tanks at three temperatures, 25, 40 and 60°C for 15 months. Water was pumped from the Brest Estuary, with no treatment except a particle filter, and was continuously renewed. Three 50 x 50 mm² coupons were immersed at 25 and 60°C, six at 40°C, as the latter was the temperature used for specimen aging. All

coupons were dried in an oven at 40°C to constant weight before immersion. Weight gains were measured on a Sartorius™ balance. Composite substrate weights were also recorded before and after immersion.

- Specimen examination

Failure surfaces were examined using both optical and scanning electron microscopy (SEM). For the latter a gold-palladium coating was applied to avoid charging and samples were studied using FEI Quanta™ 200 equipment.

Results

- Water diffusion kinetics in bulk adhesive

Weight gain measurements made on square coupons of adhesive are shown in Figure 4 for immersion in natural seawater at 25, 40 et 60°C for 15 months. Saturation levels are around 4% by weight at 60°C, 3% at 40°C and 2.5% at 25°C. The behaviour at 25 and 40°C is roughly Fickian with a stable plateau, while at 60°C there is an increase then a drop in weight gain. This higher temperature is close to the adhesive dry Tg, so the lower temperature of 40°C was used for subsequent aging conditionning in the remainder of the study.

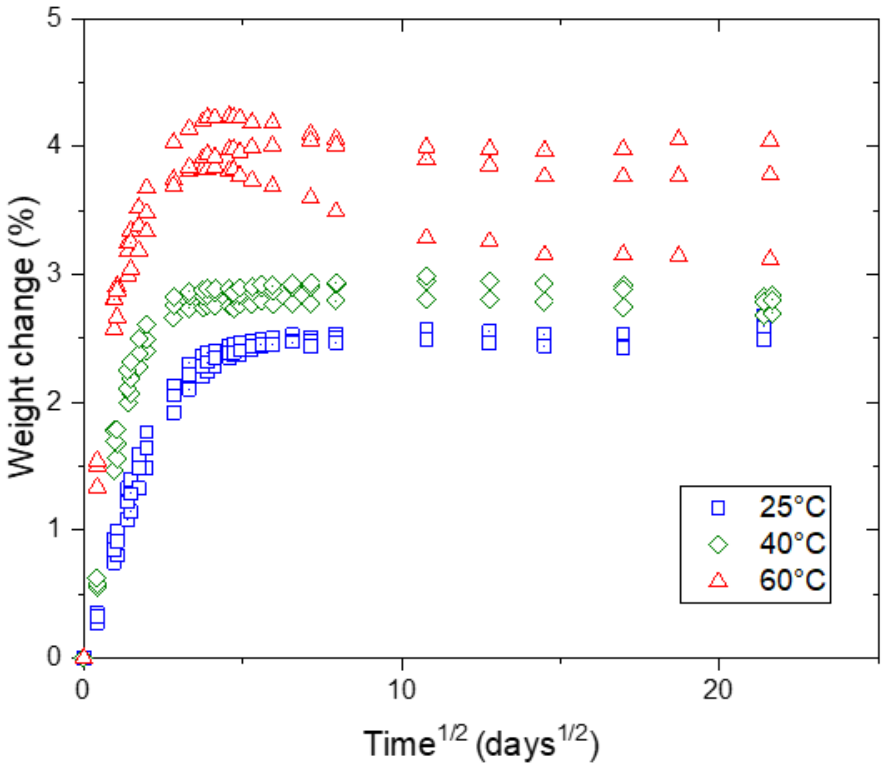


Figure 4. Weight gain plots versus square root of time, all bulk adhesive coupons in natural seawater at 3 temperatures. All data points from 9 coupons.

Three additional samples aged in seawater at 40°C until saturation (4 weeks) were then dried in an oven at 40°C for 4 weeks to examine reversibility. Figure 5 shows their weight gain then a net weight loss after drying of around 0.4%.

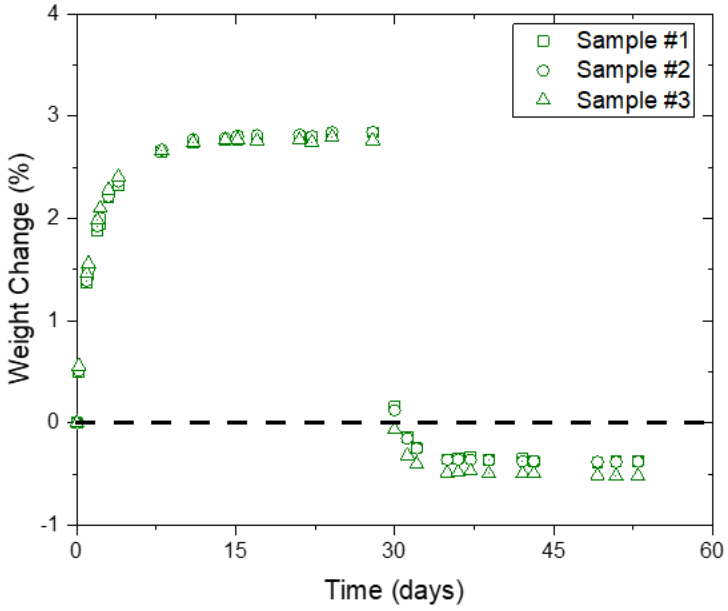


Figure 5. Weight changes during immersion then drying, both at 40°C, on the same three adhesive specimens, plotted with respect to initial dry weight.

- Influence of water on bulk adhesive properties

Adhesive dogbone specimens were tested after different aging periods, both in the wet condition and after drying to constant weight. Figure 6 shows examples of typical stress-strain plots for reference and wet tests. There is a clear tendency towards lower stiffness and strength and more ductile behaviour after immersion.

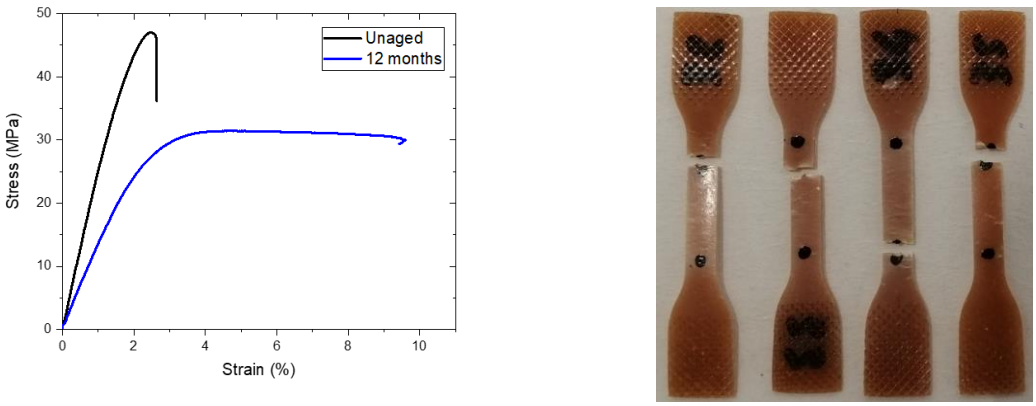
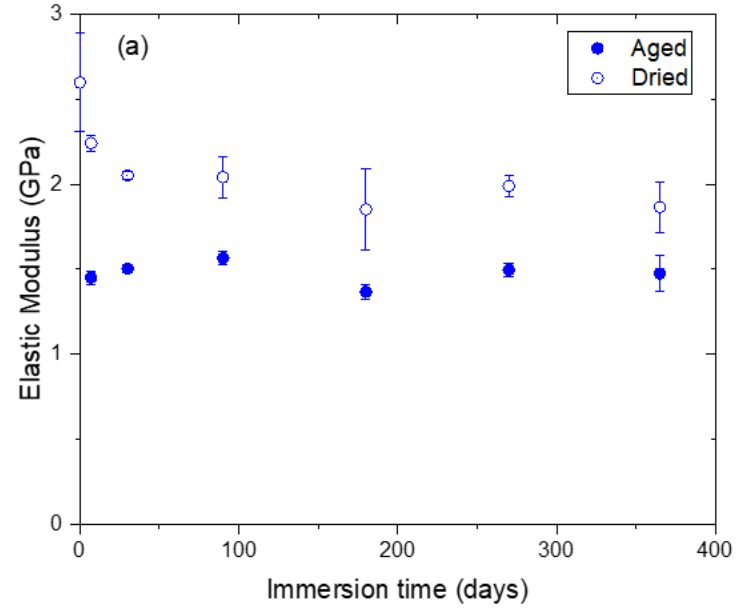
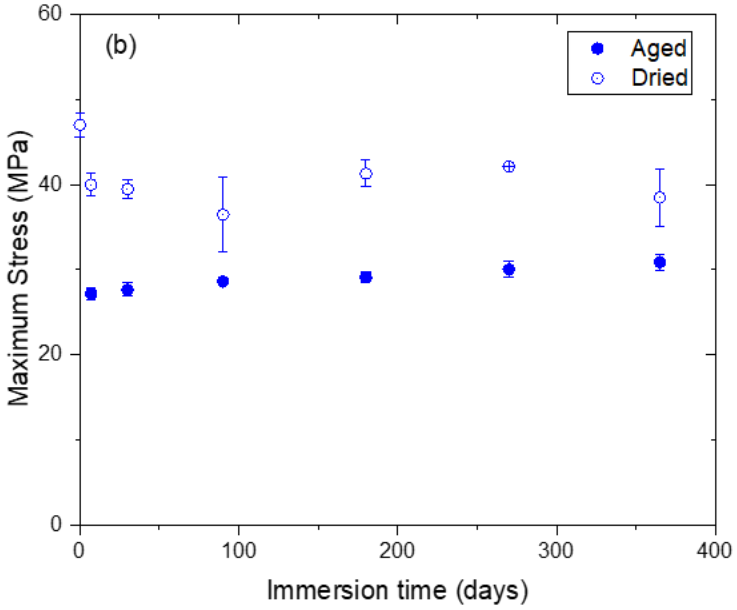


Figure 6. Tensile tests on bulk adhesive specimens.

Left: Examples of tensile stress-strain plots for bulk adhesive, unaged and after 12 months in seawater at 40°C. Right: Adhesive tensile samples (dumbell length 50mm) tested after 12 months' immersion.

Figure 7 summarizes the adhesive elastic modulus, break stress and failure strain for each condition.





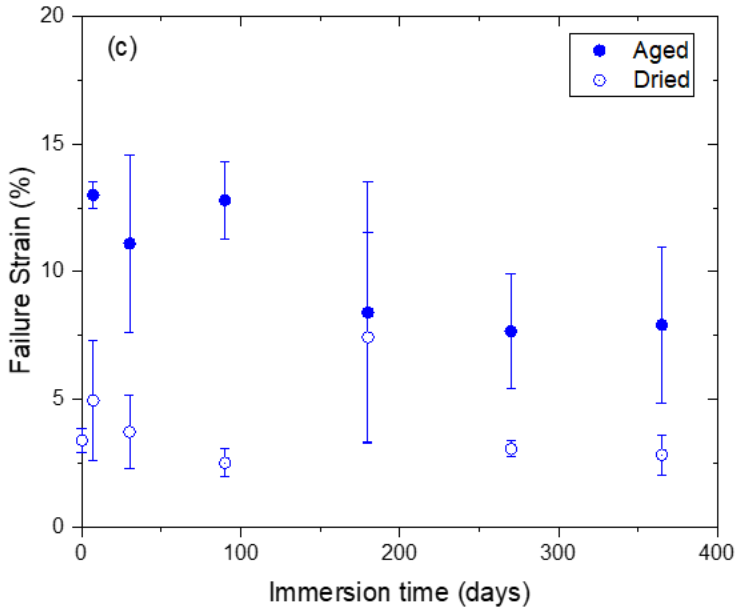


Figure 7. Adhesive tensile properties after immersion 40°C.

a) modulus, b) maximum stress, c) failure strain.

These results show that the adhesive is significantly affected by immersion in seawater, which induces a rapid drop in modulus and strength but an increase in strain to failure. This change in behaviour is consistent with a plasticization mechanism, which is reversible after drying. However, the properties after drying do not recover completely, they remain 10-20% below the initial properties. This indicates that there may be additional degradation mechanisms acting. Indeed, the weight loss after drying is greater than the initial weight gain (Figure 5), suggesting that small molecules may have been leached out. Nevertheless the tensile properties are quite stable, even after one year in seawater at 40°C.

It is interesting to compare these results with those for a common marine epoxy adhesive (Araldite™ 420) immersed in seawater at 40°C until saturation in a previous study using the same immersion tanks [37]. The epoxy was post-cured at 115°C and its weight gain at saturation was 4%, compared to around 3% for the acrylic. The unaged tensile properties shown here, modulus and strength, are similar, Table 2, the epoxy is more ductile. After saturation in seawater the acrylic strength is higher but the epoxy can achieve higher failure strains. The epoxy adhesive specimens recovered all their unaged properties after drying, the property reductions were only due to plasticization.

	Dry, before immersion			Seawater saturated		
Adhesive	Tensile Modulus GPa	Tensile strength, MPa	Break strain, %	Tensile Modulus GPa	Tensile strength, MPa	Break strain, %
Epoxy [37]	1.85	42	7	0.97	18	20
Acrylic	2.60	48	3	1.50	28	7

Table 2. Comparison between influence of seawater saturation on epoxy and acrylic marine adhesives.

- Influence of water on adhesively bonded composite samples

Adhesively bonded specimens with dry glass or carbon fibre reinforced composite substrates were tested after immersion in seawater at 40°C for periods up to 12 months. Figure 8 shows the apparent shear stress values at failure, based on the applied load divided by bonded surface area. The initial failure loads are slightly higher for the carbon composite assemblies but after 9 months in water the residual break stresses are similar for both types of assembly. The glass/epoxy assembly appears to be quite insensitive to immersion, after one year the values are close to the initial unaged scatter band. There is more scatter in the carbon specimens, with one particularly low value after 3 months.

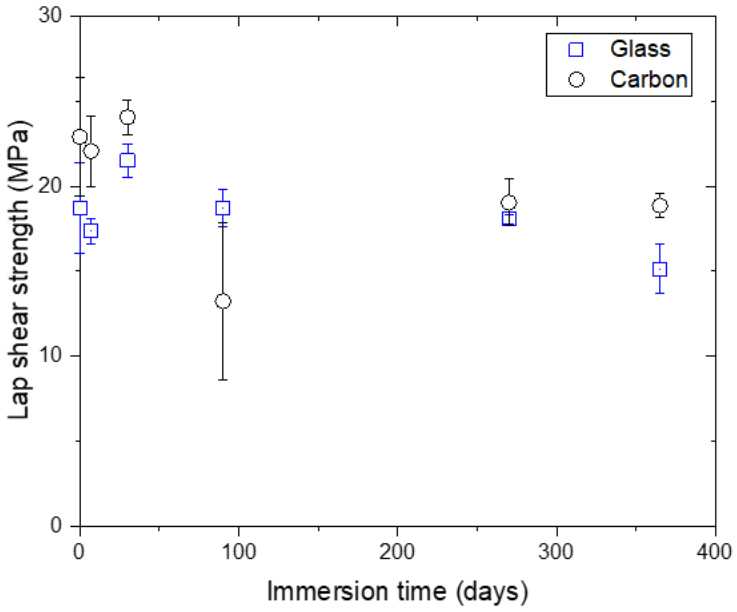


Figure 8. Influence of seawater immersion on single lap shear strengths, carbon and glass composites. Error bars show minimum and maximum values.

- Influence of water in substrates on adhesive bonding behaviour

Results from gravimetric studies of the glass and carbon fibre composite substrates are shown in Figure 9.

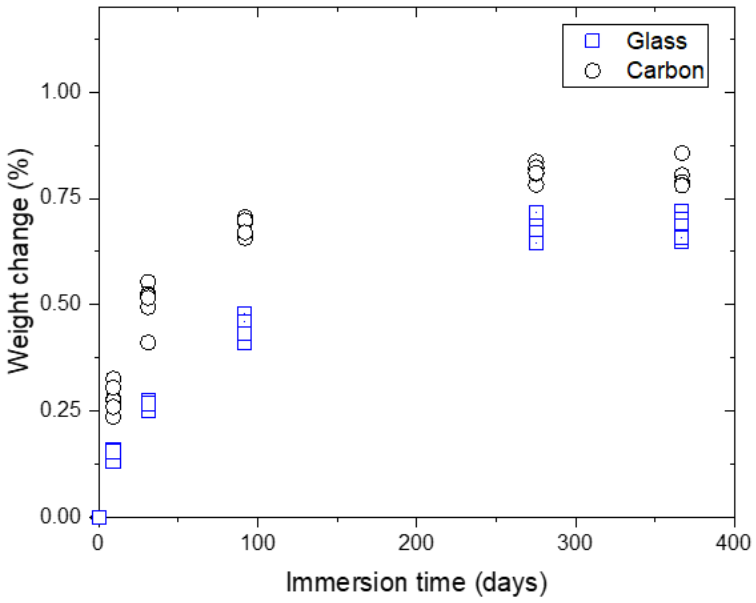


Figure 9. Weight gains of composite substrates versus immersion time in seawater at 40°C, measurements made just before bonding.

Figure 9 shows that water uptakes in both types of substrate have reached similar saturation plateau levels after 12 months in seawater at 40°C. The results from lap shear tests on specimens bonded after different substrate aging times in water at 40°C are shown in Figure 10.

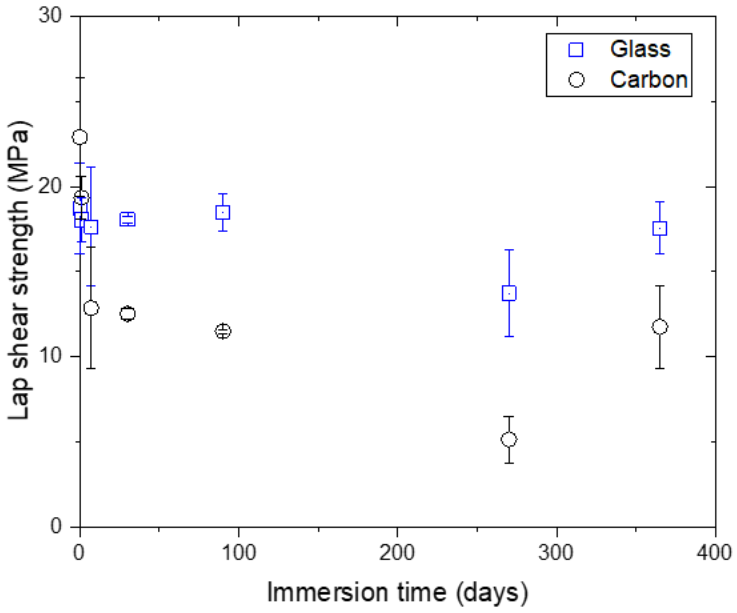


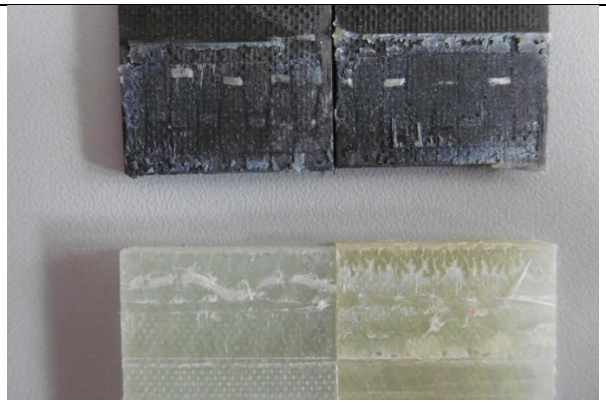
Figure 10. Influence of substrate immersion time before bonding on lap shear strength

In this case the substrates contain different amounts of water when the tests are performed but the adhesive layer is relatively dry. The behaviour here is rather different to that in Figure 8. The glass composite assemblies are not sensitive to substrates which have been immersed for up to 12 months; the lap shear strengths for saturated substrates are within the initial unaged scatter band. The carbon composite assemblies bonded with substrates which were saturated with water show a different response. When substrates are wet even for a short time the assembly strengths drop by around 40%. Nevertheless, after immersion of the substrates for 12 months in seawater at 40°C, the residual strength remains at around 50% of the initial dry value.

Discussion

It is of interest to investigate possible reasons for the difference between the behaviours of assemblies with the two types of substrate. First, there has been considerable discussion in the literature in the past on the existence of a critical minimum amount of moisture which is required before debonding occurs at adhesively bonded interfaces [1, 38, 39]. Most previous work was focussed on epoxies but a study by Tan et al. of a model PMMA bonded to glass indicated a critical moisture constant at which fracture energy dropped significantly [40]. It was postulated that for a certain amount of water both swelling of the adhesive and moisture accumulation at the interface could result in weakening of the joint. However, here the drop in strength for the carbon assemblies is noted from the first immersion so this does not appear to provide an explanation.

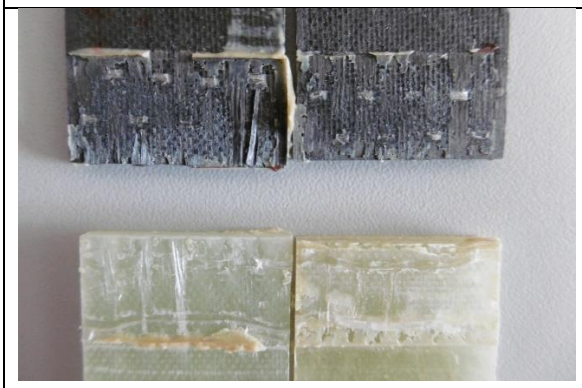
Examination of fracture surfaces may provide an indication of the difference between the residual strengths after bonding to wet adhesives. Examples of failure modes of bonded assemblies are shown in Figure 11.



Unaged reference

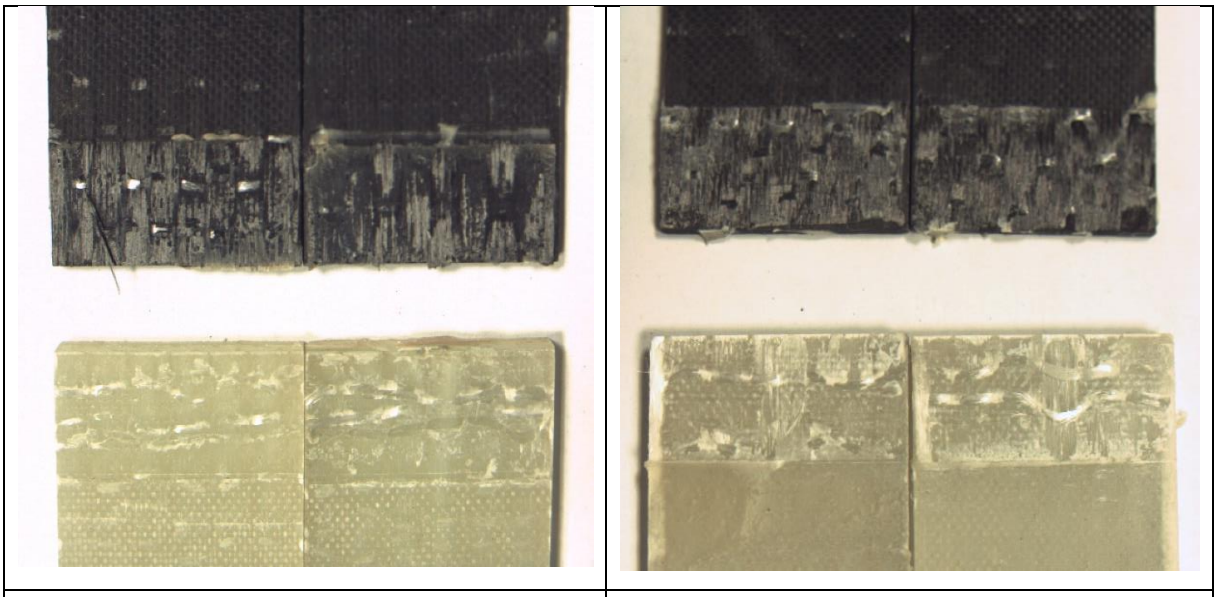
Assemblies immersed 3 months

Substrates immersed 3 months then bonded



Assemblies immersed 9 months

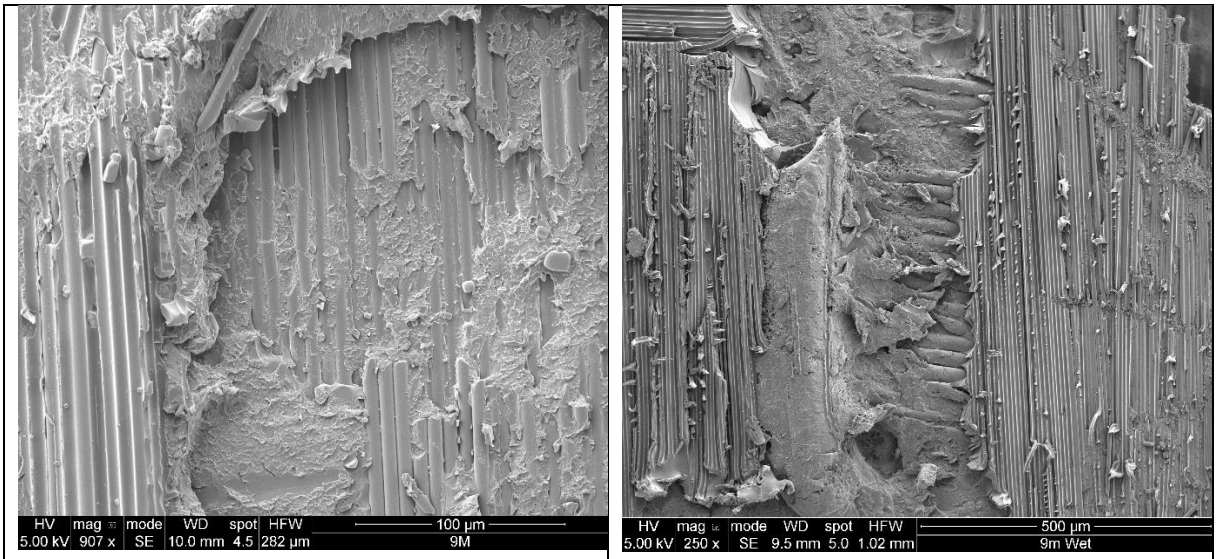
Substrates immersed 9 months then bonded



Assemblies immersed 12 months	Substrates immersed 12 months then bonded

Figure 11. Examples of fracture surfaces for carbon (upper) and glass (lower) composite assemblies

At this scale all the failures appear to be cohesive rather than adhesive. There is adhesive remaining on all substrates, with very little evidence of composite damage. The wet glass substrate surfaces show more patchy adhesive residues while dry bonded surfaces are smoother. There is also clear evidence of the presence of stitching thread, particularly on the carbon substrates. At higher magnification SEM images reveal the remains of the deformed adhesive layer (Figure 12a), and the fibre imprints above and below the adhesive (Figure 12b). In the centre of the latter image the larger diameter stitching fibres are also visible; they appear to be well-bonded to the matrix.



(a)	(b)

Figure 12. Scanning electron micrographs of 9 month aged carbon/epoxy substrate assembly after test.

The majority of the SEM fracture surfaces examined showed good bonding and adhesive deformation, Figures 11 and 12, which does not explain why the carbon substrates are more sensitive to wet aging before bonding than the glass substrates. As noted previously there are differences in the constituent materials of these composite substrates so one might expect these to affect the bonding. The first difference is the nature and properties of the reinforcing fibres. The local stress state in SLS specimens depends on the mismatch between substrate and adhesive stiffness [41]. However, while the use of carbon rather than glass reinforcement may affect the stress state during loading of the assemblies it should not affect the relative loss in properties versus substrate aging time as their stiffness is governed by the unidirectional fibre reinforcement. There is also a difference in the stitching threads, which maintain the unidirectional fibres together; the glass reinforcement contains around 15 g/m² of polyester stitching, while the carbon composite is stitched with 7 g/m² of glass fibres. The latter are clearly visible on the fracture surfaces in Figure 11. The influence of stitching on composite properties has been studied in some detail during the developmen of non-crimp fabrics, and it can affect out-of-plane properties [42]. There is no obvious reason why these small amounts of stitching would only affect the ability of the carbon composites to resist lap shear loading after seawater immersion and the cohesive nature of the failures suggests that it is probably not a factor. A published study on SLS carbon composite assemblies indicated that at high water contents after salt water immersion significant strength reduction occurred [43], but the main failure mechanisms in that work were interlaminar and intralaminar substrate cracking, which were not observed here.

Finally, another possible difference is that the nature of the substrates may affect the adhesive cure. Acrylic adhesives tend to generate an exotherm during cure and this may be affected by the thermal properties of the substrates. In order to examine this, samples of adhesive were removed from fracture surfaces and analyzed by DSC. Table 3 shows the results (mean values for 2 or 3 samples per condition).

Adhesive sample source	Condition	Tg, °C
Bulk adhesive	Dry	71
Bonded glass composite joint	Initial dry	63
	Aged 12 months seawater	61
Bonded carbon composite joint	Initial dry	45
	Aged 12 months Seawater	60
Wet glass substrate joint	Bonded after 12 months substrate immersion	49
Wet carbon substrate joint	Bonded after 12 months substrate immersion	53

Table 3. Results from calorimetry (DSC) on adhesive samples taken from fracture surfaces.

These values first indicate that the adhesive layers in the composites are less highly cured than the bulk adhesive. The adhesive in the glass composites bonded dry change little after aging but significantly lower Tg values are found when the substrates were soaked before bonding. For the carbon/epoxy assemblies the initial Tg values are significantly lower than those of the adhesive in the glass composite assemblies but post-cure during aging. Again, as for the glass, when the adhesive is bonded to wet substrates the Tg values are significantly lower for both types of substrate. The change in substrate does therefore affect the cure state of the adhesive. Further study of this effect would help to clarify the different mechanical responses after wet bonding.

Conclusion

This study has addressed three questions essential to the evaluation of this acrylic adhesive for marine applications:

First, tests on dogbone adhesive specimens indicate that the acrylic adhesive undergoes plasticization during seawater immersion. This is mostly reversible, and after one year in seawater at 40°C the adhesive retains 65% of its initial tensile strength.

Second, immersion in seawater at 40°C for up to one year hardly affects the lap shear strength of bonded assemblies of glass or carbon fibre reinforced epoxy composites. These two first results suggest that this is an interesting adhesive for marine applications.

Third, this acrylic adhesive can be used to assemble wet glass and carbon fibre composites saturated in seawater. Assemblies of saturated glass composite substrates achieved 100% of unaged strength, regardless of substrate immersion time up to 12 months, while saturated carbon composite assemblies retained around 50% of unaged values. Various possible explanations for this difference in behaviour are discussed and an influence of the nature of the substrates on adhesive cure state was noted. Further work is needed to clarify this. In conclusion, this appears to be a promising adhesive for both assembly and repair of marine structures.

Acknowledgement

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