



# Seawater ageing of infused flax fibre reinforced acrylic composites

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## ABSTRACT

This paper presents results from an experimental study of the mechanical behaviour of flax fibre reinforced acrylic composites after immersion in seawater. First, in-plane design data are presented. Then, seawater diffusion kinetics are shown, the influence of seawater on design properties is quantified and flexural fatigue performance is described. Finally the results are compared with those for glass reinforced composites. Seawater saturated specimens show a large drop in stiffness (>50%) due to fibre plasticization, but smaller drops in strength (<30%). The relevance of immersion tests is discussed and an alternative unifacial exposure test is recommended for these new materials for sustainable marine applications.

## Introduction

There is considerable current interest in natural fibre composites, which may help to reduce the environmental impact of transport applications [1]. Flax fibre reinforced thermoset composites were studied some 80 years ago by de Bruyne et al [2], but in recent years a wide range of reinforcement products have become commercially available, from non-woven to prepreg, which are creating new markets for these materials. One of the other areas where natural fibre composites could bring environmental benefits is for marine structures, such as pleasure boats, for which end-of-life disposal is a growing issue [3]. In this case the composite hull structure is continuously subjected to seawater so the behaviour of these materials in the presence of water is critical. The most frequent small boat hull material is glass fibre reinforced polyester (GRP), which shows good long-term behaviour under these conditions. It is well known that natural fibres are sensitive to water so if these composites are to replace GRP and survive in the marine environment the matrix polymer must provide long term protection. Some preliminary studies with traditional marine thermoset matrix polymers suggest that it may be possible to produce a durable composite for marine applications. For example, the Gwalaz trimaran has now been sailing regularly since 2013, with a partially biosourced polyester surrounding the flax reinforcement [4]. This has demonstrated the potential for such applications but it is not a satisfactory solution for end of life management, as such composites cannot be recycled.

Thermoplastic matrix polymers such as polyolefins are an attractive low-cost alternative, but these require a major change in boatbuilding

manufacturing strategy, with high temperatures needed to reduce polymer viscosity sufficiently to fully impregnate fibres. Arkema proposed an alternative solution recently, by marketing an acrylic matrix under the Elium™ trade name since 2014. This resin has similar modulus (3.2 GPa), tensile strength (66 MPa) and failure strain (2.8%) to common marine epoxies. The advantage of this product is that it can be infused by boatyards at room temperature using existing technology but then polymerizes as a thermoplastic, opening the way to recycling. Despite the recent introduction of this resin it has attracted considerable interest, and publications on the properties of this acrylic matrix with glass and carbon fibre reinforcements have shown promising mechanical properties and durability. Boufaïda et al. were amongst the first to provide mechanical test results, for woven glass reinforced acrylic [5]. They indicated that if a sizing with chemical groups specifically aimed at creating bonds with acrylic groups was used (in this case a patented modified silane based sizing from 3B) then fatigue properties could be significantly improved. Pini et al. presented data on mode I fracture toughness [6–8], and showed high fracture energies for a carbon fibre reinforced rubber toughened acrylic compared to the composite with the standard version. Budholi et al [9]. showed improved fracture resistance for carbon/acrylic compared to carbon epoxy and similar properties in flexure [10]. Davies et al. showed excellent flexural properties for glass and carbon reinforced acrylic, before and after seawater ageing [11]. They indicated good fatigue property retention after seawater saturation [12]. There has also been interest in the use of acrylic matrix composites for wind turbine blade infusion [13,14], with particular emphasis on the reduction in manufacturing costs (capital costs, energy, faster cycle

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times) compared to traditional thermoset composites.

These first results suggest that acrylic matrix polymers may provide attractive properties for marine applications. However, if the full environmental potential of these liquid thermoplastic composites is to be realized it is clearly of interest to establish whether they can be used in combination with natural fibres such as flax, whose environmental impact has been shown by life cycle analysis to be significantly lower than that of glass fibres [15]. There has been very little work to date on applying this polymer to natural fibre composites. An exception is the study of Chilali et al [16], who tested resin infused twill flax reinforced acrylic composites. They measured tensile properties of flax and glass reinforced acrylic and epoxy; the tensile strengths of flax reinforced epoxy and acrylic were similar and both significantly lower than those of these polymers reinforced with glass. This was partly due to lower fibre volume fractions in the flax composites but void contents were also significantly higher. However, flax reinforced acrylic matrix composites showed interesting specific tensile modulus values compared to those of glass, and damage resistance under load-unload cycles also appeared promising. Those authors presented results from a water ageing study of the same materials [17]. Immersion of samples in tap water at 20 °C for up to 30 days, before testing using tensile load-unload cycles supported by acoustic emission recordings, provided information on damage initiation. Despite the relatively short ageing time their results indicated significant degradation of both flax/epoxy and flax/acrylic, with a 50% drop in modulus and 35% loss in strength after only 2 days' immersion. This indicates that wet ageing will be a key aspect to be taken into account if natural fibre reinforced acrylic composites are to reach a wider range of applications.

The present paper will examine the potential of flax fibre reinforced acrylic as a marine composite. Although many papers have described wet ageing studies of natural fibre composites (e.g [18–22].) there is very little information available which enables designers to dimension marine structures with these materials. In order to address this here, the in-plane properties required for design were measured first, using standard tensile and tests on 0°, 90° and ±45° laminates. Then these specimens were aged in natural seawater at different temperatures (25, 40 and 60 °C) for up to 15 months, and weight gain kinetics were determined. Seawater saturated specimens were subsequently tested under quasi-static loads, in order to quantify the change in design properties after wet ageing. Finally, a series of four point flexure tests was performed under both quasi-static and cyclic loading, in order to examine fatigue performance. Results are compared with published values for glass fibre reinforced marine composites and the potential of flax reinforced acrylic for marine structures is discussed. The particularly severe nature of total immersion testing of natural fibre composites is highlighted, and an alternative uni-facial test procedure is proposed.

## Materials and methods

### Materials

The reinforcement studied is a non-treated quasi-unidirectional flax (200 g/m<sup>2</sup>, 93% warp rovings, 7% weft) from Depestele (FWUD200), used in unidirectional (0°) and balanced 0/90° layouts. The resin is a 188 XO grade Elium™ acrylic from Arkema, mixed with 1.5% by weight peroxide powder catalyst (CH-50 U Perkadox™). One-metre square panels of each sequence were manufactured by room temperature resin infusion at Kaïros, Concarneau, followed by post-cure in an oven at 80 °C for 1 hour. Fibre reinforcements were dried in an oven at 30 °C, 40% relative humidity for 4 h before infusion. The physical properties of the resulting composites are described in Table 1.

Fibre volume contents ( $V_f$ ) of flax fibre composites are not easy to determine accurately. The simplest method, used initially here, is to measure density with a helium pycnometer. These values are given in Table 1. It is then possible to use a rule of mixtures to estimate  $V_f$  provided that fibre and resin density are known. Various studies have

**Table 1**

Measured material thicknesses and density, estimated fibre ( $V_f$ ) and void ( $V_v$ ) contents, glass transition temperatures ( $T_g$ ) from DSC.

Sequence	Thickness (mm)	Density (g/cm <sup>3</sup> )	Estimated $V_f$ (%)	Estimated $V_v$ (%)	$T_g$ (°C)
[0] <sub>s</sub>	4.5 ± 0.1	1.27 ± 0.01	30 ± 2	8	56 ± 4
[±45] <sub>4s</sub>	4.3 ± 0.1	1.28 ± 0.01	33 ± 2	8.5	64 ± 4
[0/90] <sub>s</sub>	4.6 ± 0.2		33 ± 2	8.5	64 ± 4

shown that flax fibre density depends on the measuring method [23]. Here a value of 1.46 g/cm<sup>3</sup> was taken for the fibre density based on [23], (a mean value between 1.39 g/cm<sup>3</sup> measured by immersion and 1.53 g/cm<sup>3</sup> measured by pycnometer), and a measured resin density of 1.19 g/cm<sup>3</sup> [11]. Based on these values and neglecting porosity the fibre contents are in the range 30–33%, and this will be shown below to be consistent with measured values of modulus.

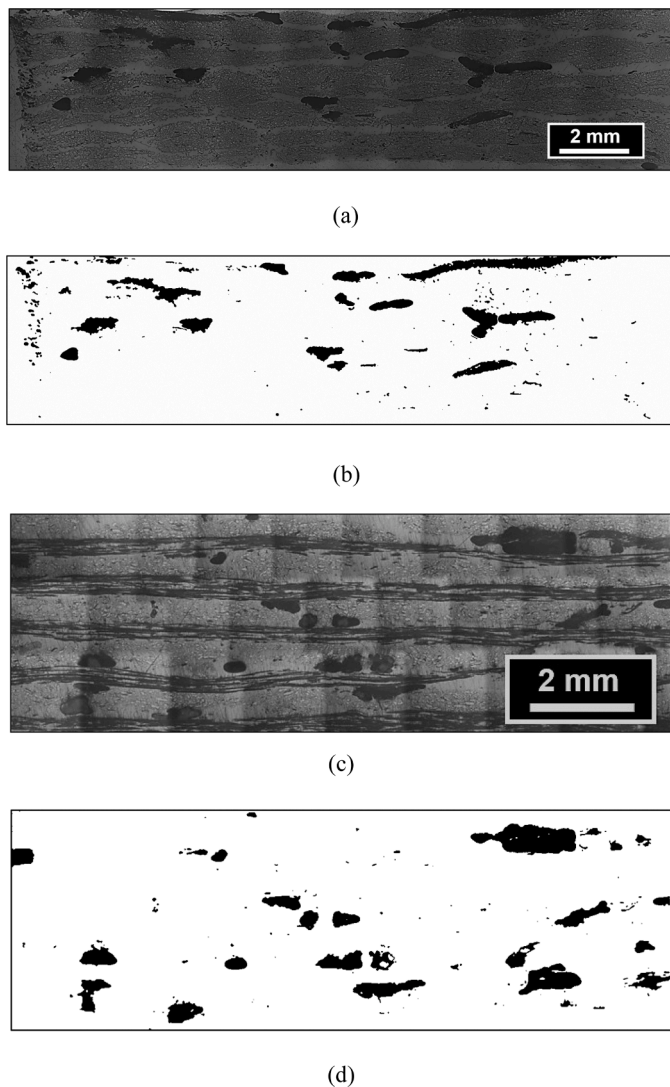
The  $T_g$  (glass transition temperature) values in Table 1, were measured by DSC (Differential Scanning Calorimetry) using TA Instruments Q200 equipment. These values were measured during the first heating cycle on specimens taken through the panel thickness, with a heating rate of 10 °C/minute. They are a little lower than those obtained in previous studies on glass and carbon fibre reinforced acrylic, for which values of 89 and 75 °C were measured respectively, after 12 h cure at 65 °C [12]. Values measured during the second DSC heating cycle were close to 90 °C indicating that the formulation was correct and that higher  $T_g$  values could probably be obtained by further post-cure, but the aim here was to produce samples under boatyard manufacturing conditions, not to optimize cure cycles. Fig. 1 shows optical microscope images of a cross-section of untested 0° and 0/90° tensile specimens, prepared by casting in resin and polishing first with papers then diamond paste down to 1 µm.

Polished sections were examined and analysed to determine void content. Fig. 1.b shows an example for the 0° composite. Void content was determined by image analysis using *ImageJ* software. The void content was estimated to be around 8% by volume. Polished sections from 0/90° specimens were also examined, Fig. 1.c, and the image after treatment for void content determination is shown in Fig. 1.d. A void content of around 8.5% was obtained for this laminate. These values are higher than those usually found in infused glass fibre composites but not unusual for natural fibre composites. For example, Chilali indicated 5% for flax/acrylic [16], Berges et al. indicated values between 5 and 8.6% for flax/epoxy prepreg composites [24], while a recent study on porosity in flax/PLA composites using a CT scanner by Kergariou et al. measured around 8% [25].

### Seawater ageing

Square 60 × 60 mm<sup>2</sup> samples (initial weights around 25 g, thicknesses given in Table 1) were dried for 1 week in an oven to constant weight at 40 °C, then immersed in seawater tanks at three temperatures, 25, 40 and 60 °C, to examine weight gain kinetics. Three samples of 0° and three of the 0/90° sequence were immersed at each temperature. These tanks are filled with temperature controlled natural seawater from the Brest Estuary, which is continuously renewed. A temperature of 40 °C was subsequently adopted to saturate specimens for mechanical tests. Continuous temperature measurements indicated a temperature variability < ±2 °C during the immersion period.

A second series of specimens was subjected to single face seawater exposure, in order to provide more representative data for a boat hull application. This was achieved by fixing 65 × 65 mm<sup>2</sup> coupons to the exterior of a smaller seawater tank, Fig. 2. The diameter of the openings in the tank wall is 50 mm, so weight gains are calculated with respect to the weight of a circular area of material of this diameter, rather than of



**Fig. 1.** a) Polished section of a 0° specimen, b) Image after analysis to highlight porosity in 0° specimen, c) Polished section of a 0/90° specimen, d) Image after analysis to highlight porosity in 0/90° specimen.

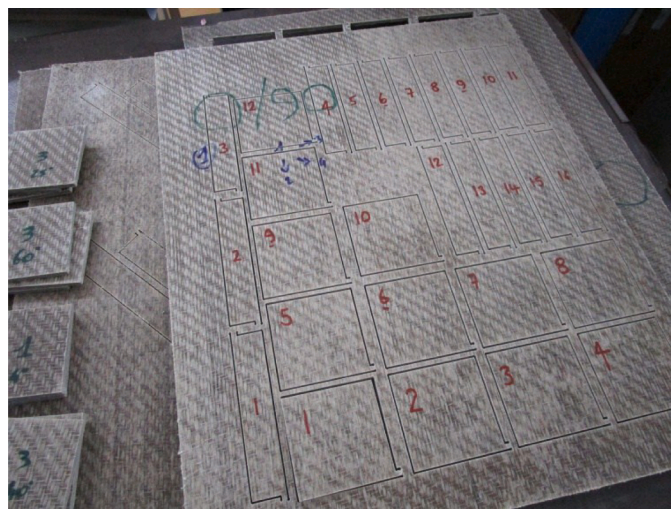
the complete square sample. This results in a weight gain correction factor of x2.15 with respect to the measured coupon weight gain. Reference specimens were immersed inside the tank during the same

period, as this tank temperature was measured but not controlled.

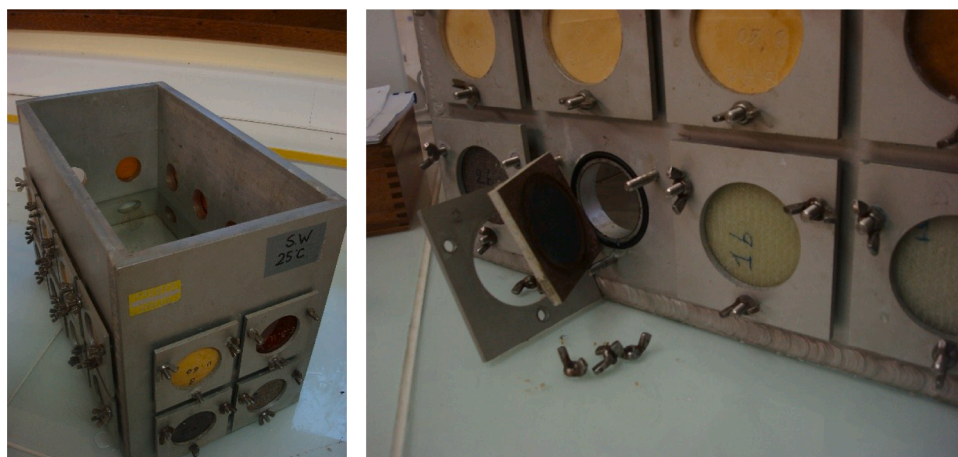
#### Mechanical test methods

Standard test methods were used to determine in-plane moduli and strengths for 0° (ASTM D3039), 90° (ASTM D3039) and  $\pm 45^\circ$  (ASTM D3518) specimens. Specimens were taken from panels using water jet cutting, Fig. 3 and dimensions of the specimens were  $250 \times 25 \times 4.4 \text{ mm}^3$ . Tests were performed under displacement control at 2 mm/minute. Longitudinal and transverse strains were measured by Digital Image Correlation (DIC) using GOM Correlate software. Also, all specimens were tabbed using glass/epoxy tabs with a sequence of  $[\pm 45^\circ]$ .

Flexural testing included short beam shear (ASTM 2344), and four point flexure (ASTM D790). The latter was performed under both quasi-static (displacement control 5 mm/minute) and cyclic loading (load control, 2 Hz,  $R = 0.1$ ) on a Zwick 25 kN capacity test machine. Specimen geometry was  $(140 \times 24) \text{ mm}^2$ . Distance between supports was 120 mm, with 60 mm between loading points, the radius of supports and loading points was 5 mm.



**Fig. 3.** Specimens for flexure and weight gain (top panel) and  $\pm 45^\circ$  (lower panel) after water jet cutting. Panel dimensions  $500 \times 500 \text{ mm}^2$  (0/90° panels).



**Fig. 2.** Unifacial seawater exposure tank.



## Results

### Unaged properties

First a set of design data was produced by tensile tests on  $0^\circ$ ,  $90^\circ$  and  $\pm 45^\circ$  specimens. These are standard test results, but due to the recent introduction of this acrylic matrix few such data are available for flax/acrylic composites. Some published tensile results for infused woven flax/acrylic with 37% flax by volume indicated modulus and strength values of 14 GPa and 120 MPa [16].

Fig. 4 shows the stress-strain plots. Two axial modulus values, respectively equal to 14.4 and 10.8 GPa can be determined corresponding to low and high strains on the UD specimens, as noted elsewhere [26]. These values allow us to confirm the fibre volume fraction estimated initially from density measurements. Here, using the rule of mixtures based on the moduli from the constitutive elements ( $E_f = 48$  GPa [27] and  $E_m = 3$  GPa [11]) and the modulus of the  $0^\circ$  composite measured to be 14.4 GPa, and neglecting porosity, we obtain a value of 14.5 GPa for a fibre volume fraction around 32%, i.e. quite similar to that obtained using density measurements. It should be noted however, that the accuracy of such estimations for natural fibre composites has been examined in detail in recent papers [28,29]. Given the much higher uncertainty in input parameters ( $V_f$ ,  $V_v$ ,  $E_f$ ) compared to glass and carbon fibre composites these should be treated as indicative only.

A set of flexural tests was then performed on the  $0^\circ$  and  $0/90^\circ$  materials Fig. 5. shows examples of stress-displacement plots. Finally some cyclic flexural tests were performed on both these materials, Fig. 6. Failure in flexure occurred in tension below the loading points.

### Seawater ageing kinetics

Fig. 7 shows the weight gain plots for square samples immersed at 25, 40, and  $60^\circ\text{C}$  for 16 months. Raising the water temperature from 25 to  $40^\circ\text{C}$  increases the weight gain rate, but a further increase does not

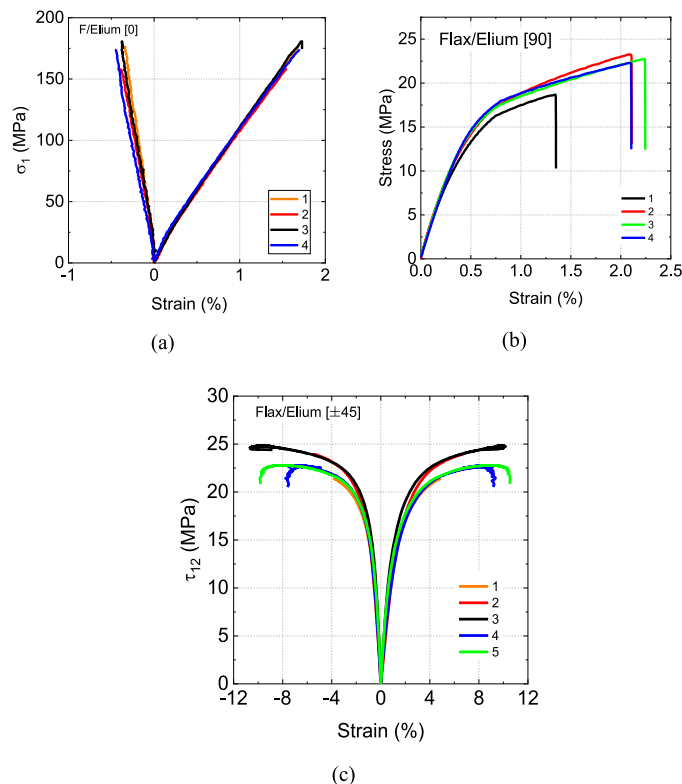


Fig. 4. Tensile stress-strain plots for unaged a)  $0^\circ$ , b)  $90^\circ$  and c)  $\pm 45^\circ$  specimens.

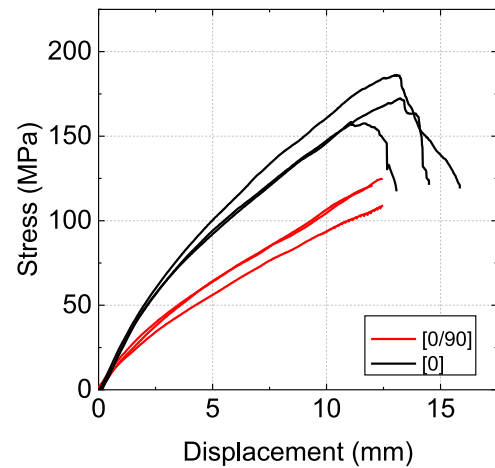


Fig. 5. Four point flexure plots, unaged,  $0^\circ$  (black),  $0/90^\circ$  (red).

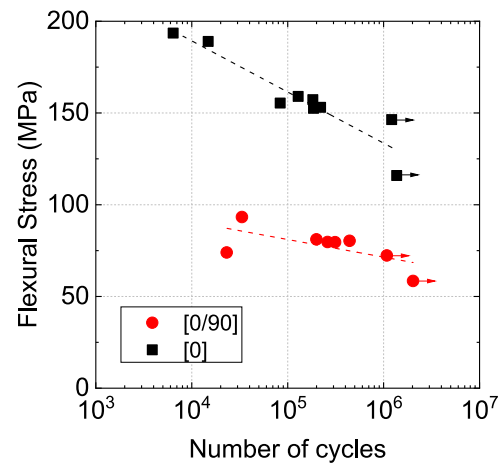


Fig. 6. Flexural fatigue plot, unaged  $0^\circ$  and  $0/90^\circ$  specimens.

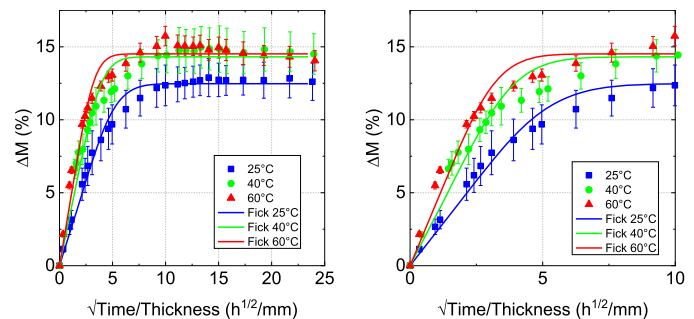


Fig. 7. Examples of weight gain plots, seawater immersion at 3 temperatures, 15 months' immersion, and close-up of start of immersion, unidirectional.

result in a significant change. This may be because the  $60^\circ\text{C}$  temperature is within the dry glass transition range of the matrix. Although the fit to the Fickian behaviour often found in polymers and composites is quite approximate here this does allow diffusion coefficients to be estimated, Table 2. There appear to be two slopes, corresponding to different diffusion mechanisms. This would not be surprising given that, in contrast to glass and carbon fibre composites, here both fibres and matrix absorb water. There appears to be a stabilization of the weight uptake around 12% at  $25^\circ\text{C}$  and 15.5% at 40 and  $60^\circ\text{C}$ .

Previous tests on unreinforced acrylic matrix by the authors have

**Table 2**

Diffusion kinetics parameters in seawater, (D: diffusion coefficient,  $M_{\text{sat}}$  mass at saturation) based on Fickian behaviour.

	Temperature	25 °C	40 °C	60 °C
Flax/Eluim	D (m <sup>2</sup> /s)	$3.45 \cdot 10^{-12}$	$6.71 \cdot 10^{-12}$	$9.02 \cdot 10^{-12}$
	$M_{\text{sat}}$ (%)	12.8	14.5	15.1
Neat Resin [11]	D (m <sup>2</sup> /s)	$0.55 \cdot 10^{-12}$	$1.39 \cdot 10^{-12}$	$4.23 \cdot 10^{-12}$
	$M_{\text{sat}}$ (%)	1.87	1.85	1.90

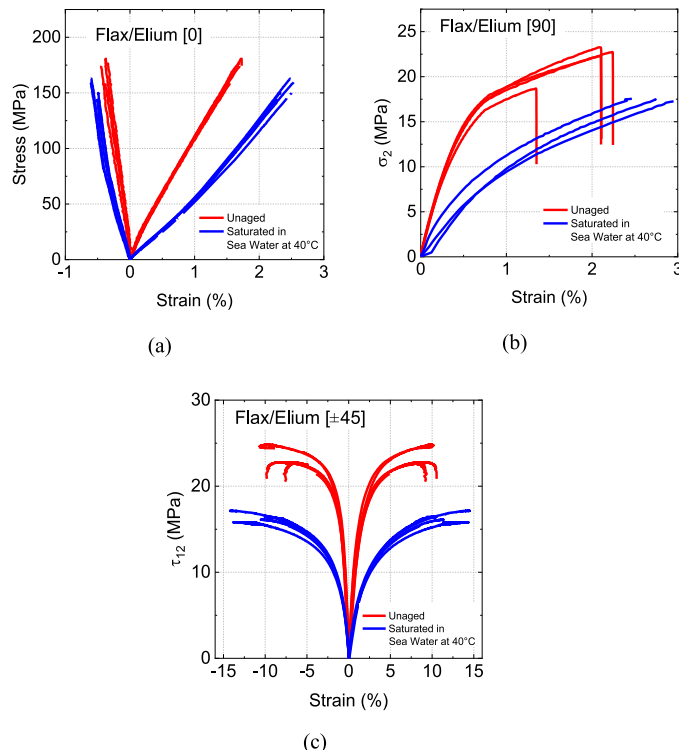
indicated a saturation weight gain around 1.9% [11]. However, this value does depend on the particular resin and catalyst used. Other authors found a saturation level of 1.64% in distilled water at 40 °C [30]. As expected, the majority of the weight gain here is associated with the flax fibres, this will be discussed further below. Tensile properties cited in [31] indicated losses in stiffness of flax fibres from 60 to around 20 GPa after soaking, but much smaller strength reductions.

#### Quasi-static properties after immersion

After saturation of test coupons at 40 °C (2 months) these were tested to failure. Fig. 8 shows examples of the stress-strain plots for each loading case.

All the in-plane properties of this material are affected by water Table 3. summarizes the values measured, and the percentage changes compared to unaged properties.

There is a strong influence of seawater on stiffness values (−60%) and a rather smaller influence on strengths (around −20%). This is consistent with the flax fibre changes noted in [31]; the results here suggest that water strongly affects the fibre modulus, emphasizing the essential role of the matrix polymer in protecting the fibres from moisture ingress. Composite strength changes after immersion are more complex, and less sensitive than stiffness to water. Scanning electron microscopy was employed to examine 90° and ±45 °C specimen fracture surfaces after ageing. This revealed a rather brittle matrix and significant fibre damage. Two examples are shown in Fig. 9 below.



**Fig. 8.** Tensile behaviour after seawater saturation at 40 °C.

**Table 3**

Unaged and saturated material properties measured on unidirectional composites.

Property	Unaged	Seawater saturated	% change after ageing
$E_1$ (GPa) 0° Modulus	$14.4 \pm 1.1$	$5.2 \pm 0.2$	−64
	* 10.8 ± 0.4**	$7.5 \pm 0.2$	−31
$E_2$ (GPa) 90° modulus	$3.3 \pm 0.2$	$1.4 \pm 0.3$	−58
$G_{12}$ (GPa) In-plane shear modulus	$1.1 \pm 0.2$	$0.5 \pm 0.1$	−56
$\nu_{12}$ In-plane Poisson's ratio	$0.20 \pm 0.08$	$0.24 \pm 0.07$	+20
$\sigma_1$ (MPa) 0° tensile strength	$173 \pm 10$	$153 \pm 8$	−12
$\sigma_2$ (MPa) 90° tensile strength	$22 \pm 2$	$17 \pm 1$	−23
$\tau_{12}$ (MPa) In plane shear strength	$24 \pm 1$	$16 \pm 1$	−33
$\tau_{13}$ (MPa) ILSS	$14 \pm 1$	Invalid failure	/
$\sigma_{if}$ (MPa) 0° flex strength	$172 \pm 14$	$100 \pm 15$	−42

\* First slope.

\*\* Second slope.

#### Cyclic behaviour after immersion

Cyclic four point flexural tests were then performed and Fig. 10 shows the results.

Failure modes in flexure are shown in Fig. 11. The unaged samples failed in tension below the loading points, whereas the aged samples failed in local compression with no sign of tensile failure.

#### Discussion

First, the set of unaged tensile properties is compared in Table 4 with those of a more traditional glass/epoxy marine composite, manufactured using a similar infusion process [32], and a glass/acrylic material tested previously [11]. The latter were tested using the same equipment and test protocols as the flax/acrylic.

This Table indicates that before immersion the natural fibre composite stiffness properties measured here are around one third of those of the glass composite. The tensile strengths are also much lower, around 15%. A first reason for this difference is the lower flax fibre volume content, around 30–33%, compared with around 51% for the glass reinforced composite. The high porosity of the flax based composites produced by infusion should also be noted. Voids affect the properties of all composites (e.g [33].), but natural fibre composites are particularly susceptible to void formation [34]. This is encouraged by inherent humidity in fibres and variable fibre geometry. Increasing pressure during manufacturing can reduce void content, and hot press forming may produce better quality materials [35], but for marine applications infusion is the most popular forming method allowing complex parts to be produced with low investment. On the other hand, the density of the flax composite at 1.28 is significantly lower than that of the infused glass fibre composite (1.81), so specific properties, also shown in Table 4, become more attractive. These results indicate that in order to use this material to replace a glass fibre reinforced composite in an application dimensioned for flexural stiffness would require a thicker flax composite. However, as flexural stiffness increases with the cube of thickness the increased amount of material required may be acceptable. For strength-based design a satisfactory replacement may be more difficult to achieve.

The second property of particular interest for highly loaded marine applications such as tidal turbine blades is their fatigue strength. The data shown in Fig. 10 indicate that while the unaged fatigue strength is quite high (around 75% of the static strength at 1 million cycles) these values drop significantly after seawater saturation. There are relatively few data available for fatigue of flax reinforced composites. Shah and

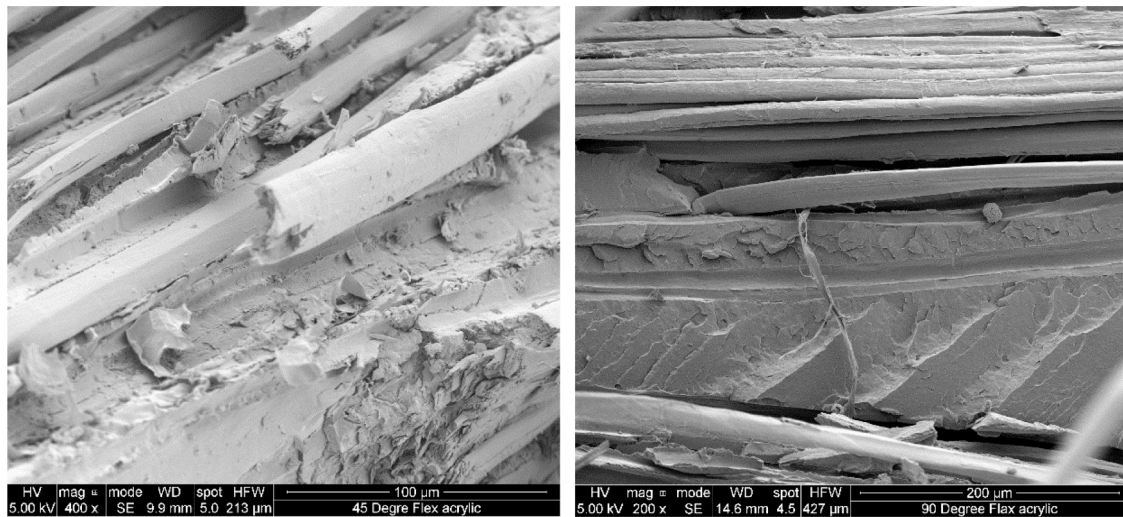


Fig. 9. SEM images, aged 45° (left) and 90° (right) fracture surfaces.

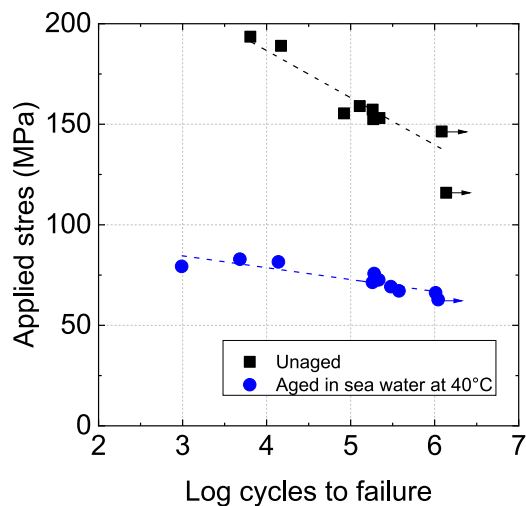


Fig. 10. Flexural fatigue S-N plots for unidirectional flax/acrylic before and after seawater saturation. Arrows indicate run-out specimens after  $10^6$  cycles.

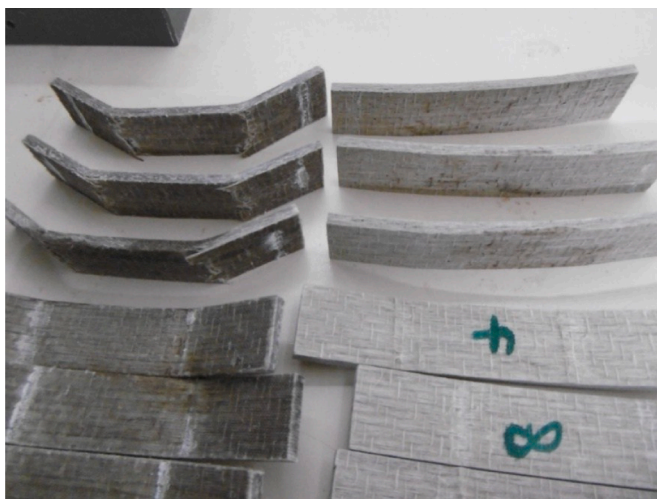


Fig. 11. Flexure specimens after cyclic testing.

Table 4

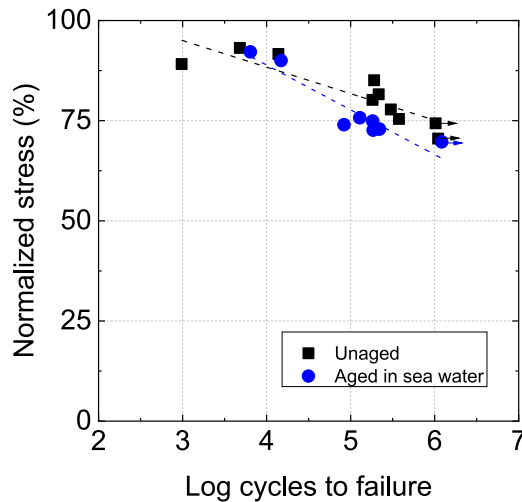
Comparison between tensile properties of flax and glass fibre reinforced composites.

Material	Modulus, GPa	Strength, MPa	Specific modulus E/ $\rho$	Specific strength $\sigma/\rho$
Flax/Acrylic				
0°	14.4	173	12	147
0/90°	7.8	97	6.1	76
Glass/epoxy [32]	42	1150	23	635
0°	19	595	10.5	350
0/90°				
Glass/acrylic [11]	25	500	12	245
0/90°				

colleagues were amongst the first to present fatigue data and they showed that although the absolute fatigue performance of GFRPs is far superior to plant fibre composites, the fatigue strength degradation rates of the latter were actually lower [36]. Bensadoun et al [37], showed the strong influence of flax fibre architecture on fatigue performance of epoxy composites. Liang et al [38], examined damage development during fatigue behaviour of 0°, 90°, 45° and 0/90° laminates and also showed that S-N plots normalized by static break stress were quite similar for the different orientations. This normalization exercise was performed on the flexural fatigue data obtained here, Fig. 12, and the normalized plots before and after seawater ageing are also quite similar. In one of very few previous studies on fatigue behaviour of flax composites after wet ageing Bergès et al [24] tested prepreg-based flax/epoxy composites before and after conditioning at 70 °C and 85% RH. Surprisingly they found that tensile fatigue strength of the wet materials improved compared to unaged behaviour. The results shown here suggest that the compression response of flax composites is more sensitive to moisture under cyclic loading than the tensile response. There has been very little work on the sensitivity of compression properties of flax composites to water, these results indicate that more work is required in this area.

It is also interesting to examine the role of the fibres during immersion. Reported values of the amount of water that flax fibres and their composites can take up vary greatly Table 5, shows some examples.

For example, Symington et al. indicated flax fibre weight gains at saturation after immersion of over 100% by weight [31], while other authors showed values in the range 40 to 60% [39-41] under different moisture conditions. Measurements of fibre weight gain are not simple, and may overestimate water ingress; it is difficult to separate water



**Fig. 12.** Normalized S-N plots for flax/acrylic before ageing and after saturation.

**Table 5**

Examples of weight gains of flax fibres and flax reinforced composites during wet ageing.

Material	Composite ( $V_f$ )	Weight gain at saturation, %	Reference, Condition
Flax fibres	-	120	[31] immersion
	-	43	[39] 100%RH
	-	50	[40] immersion
	-	63	[41] immersion
Flax composite Immersion 25 °C	Flax/resin (38%)	9.6	[42]
	Flax/Epoxy (32%)	7.3	[17]
	Flax/Acrylic (37%)	19.8	[17]
	Flax/Acrylic (37%)	13.5	[43][44]
	Flax/Epoxy (51%)	12.8	Present work
	Flax/Epoxy (40%)		
	Flax/acrylic (30–33%)		

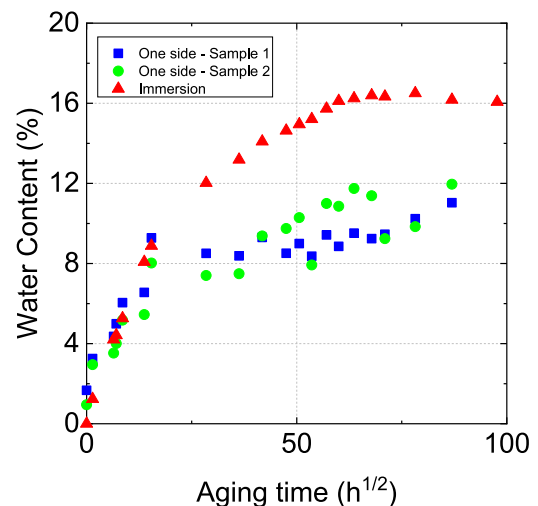
within the fibres from water on their surfaces and within the lumen. In the present work if we assume that the composite water uptake is distributed between the matrix and the fibres, and that the matrix saturates at 1.9% by weight, then the fibre weight gain at saturation, based on a  $V_f$  of 32%, would be expected to be around 40%. Although this is similar to the value found in [39] this value cannot be successfully applied to the results from the other studies reported in Table 5. Indeed, if only fibre absorption is assumed to control composite weight gain (and supposing that fibre volume fractions are correct) then values ranging from 20 and to 40% would be needed to accommodate the measured values. This underlines the difficulty in examining the durability of natural fibre composites compared to the case for traditional composites, for which in many cases composite weight gain can be accurately predicted from matrix weight gain.

An additional point of importance for marine applications is that the standard procedure for studying water ingress in traditional composite materials is to completely immerse square coupons. There is known to be an edge effect but as it is the matrix which is sensitive to moisture in most composites the effect is small unless very small coupons are studied, and its influence can be estimated [45]. Applying this approach to natural fibre composites allows rapid saturation, but the ingress at the coupon edges is accelerated due to the exposed fibre ends. As a result, the diffusion kinetics are not representative of marine applications such as boat hulls, which are only exposed to water on one face. Some

additional tests were therefore performed on these flax/acrylic materials with seawater applied to a circular area on only one coupon face (the set-up is shown in Fig. 2), thus avoiding the influence of free edges. Weight gains using this configuration are shown in Figure 13 for an immersion in 20 °C seawater for 12 months followed by 6 months' drying in an oven at 40 °C. It may be noted that the initial slopes are similar but the stabilized amount of water is significantly lower than for the fully immersed coupons. The stabilized amount of water will depend on the environmental condition at the unexposed face, as this will control the final profile through the coupon thickness. If we assume a dry unexposed face and a linear profile through the thickness at saturation the amount of water for the uniaxial exposure condition would be expected to be around half that for the full immersion, neglecting edge effects. In Fig. 13 there is some scatter, the tank has to be drained and samples removed for each measurement which takes some time, but the saturation level is around 10%. This indicates that the unexposed face condition was not dry, it was probably closer to 50% relative humidity, so the moisture content there is not zero. In further work it would be interesting to examine the influence of this condition by performing tests with the tank in a climatic chamber.

For applications such as boat hulls, where water exposure is limited to one side of the structure, diffusion kinetics from this type of uniaxial test are clearly more relevant and would allow more realistic lifetime predictions.

Finally, a major reason for studying this acrylic matrix resin is that its thermoplastic nature can be obtained using the traditional low temperature infusion moulding methods commonly used in boatyards, thus opening the way to recyclable marine composites. It is therefore important to consider how this recycling can be achieved. A recent study by Cousins [46,47] proposed four approaches to recycling glass fibre reinforced thermoplastic composites: Thermal degradation (pyrolysis), mechanical grinding, thermoforming, and solvolysis and dissolution. The two former can be applied to thermoset composites but thermoforming was used to change the shape of acrylic composite parts (e.g. flattening curved wind blade geometries by heating to 120 °C under low pressure) and to recover the matrix monomer (heating in a solvent such as chloroform or acetone). Frej et al [48] describe a study in which carbon fibres and acrylic resin were recovered from a carbon fibre reinforced acrylic composite. A pyrolysis process allowed the depolymerisation of the acrylic matrix and recovery of matrix monomer. Distillation was used to purify the monomer and a recycled resin was synthesized. It would be interesting to examine the life cycle analysis of this procedure but it does suggest that an acrylic based composite may provide additional end of life options compared to traditional thermoset



**Fig. 13.** Comparison between uniaxial exposure and complete immersion, flax/acrylic 0°, seawater, 20 °C.



composites.

## Conclusion

This study first provides a set of design data for flax fibre reinforced acrylic composites, manufactured by infusion under boatyard conditions, both unaged and after natural sea water ageing. Water affects the static and cyclic properties of flax/acrylic composites; seawater saturation results in reductions in modulus, by 50% or more, but smaller reductions in strengths (30% or less). A single face water exposure test is proposed for marine applications such as boat hulls.

These results will allow designers to assess the potential of this material for marine applications by taking account of material changes in service. They also provide essential data for Life Cycle Analysis, which requires knowledge of the useful life of a product. This should enable the environmental impact of this new material, a natural fibre based thermoplastic, to be evaluated.

## Declaration of Competing Interest

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

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## References

- [1] M.S. Fogorasi, I. Barbu, The potential of natural fibres for automotive sector - review, *IOP Conf. Ser.: Mater. Sci. Eng.* 252 (2017), 012044.
- [2] N.A. De Bruyne, Plastic progress. Some further developments in the manufacture and use of synthetic materials for aircraft construction, *Flight* (1939) 77–79, 12 January.
- [3] M. Onal, G. Neşer, End-of-life alternatives of glass reinforced polyester boat hulls compared by LCA, *Adv. Compos. Lett.* 27 (2018) 134–141.
- [4] L. Bosser, E. Poisson, E. Grossmann, P. Davies, The first all-flax composite trimaran, *JEC Magazine* 84 (2013) 45–47.
- [5] Z. Boufaïda, L. Farge, S. André, Y. Meshaka, Influence of the fiber/matrix strength on the mechanical properties of a glass fiber/thermoplastic-matrix plain weave fabric composite, *Compos. Part A* 75 (2015) 28–38.
- [6] T. Pini, F. Briatico-Vangosa, R. Frassine, M. Rink, Fracture toughness of acrylic resins: viscoelastic effects and deformation mechanisms, *Polym. Eng. Sci.* 58 (2018) 369–376.
- [7] T. Pini, F. Caimmi, F. Briatico-Vangosa, R. Frassine, M. Rink, Fracture initiation and propagation in unidirectional CF composites based on thermoplastic acrylic resins, *Eng. Fract. Mech.* 184 (2017) 51–58.
- [8] T. Pini, F.B. Vergosa, R. Frassine, M. Rink, Matrix toughness transfer and fibre bridging laws in acrylic resin based CF composites, *Eng. Fract. Mech.* 203 (2018) 115–125.
- [9] S.K. Bhudolia, P. Perrotey, S.C. Joshi, Mode I fracture toughness and fractographic investigation of carbon fibre composites with liquid methylmethacrylate thermoplastic matrix, *Compos. Part B* 134 (2018) 246–253.
- [10] S.K. Bhudolia, S.C. Joshi, A. Bert, B.Y. Di, R. Makam, G. Gohel, Flexural characteristics of novel carbon methylmethacrylate composites, *Compos. Commun.* 13 (June 2019) 129–133.
- [11] P. Davies, P.-Y. Le Gac, M. Le Gall, Influence of sea water aging on the mechanical behaviour of acrylic matrix composites, *Appl. Compos. Mater.* 24 (1) (2017) 97–111.
- [12] P. Davies, M. Arhant, Fatigue behaviour of acrylic matrix composites: influence of seawater, *Appl. Compos. Mater.* 26 (2) (2019) 507–518.
- [13] R.E. Murray, D. Penumadu, D. Cousins, R. Beach, D. Snowberg, D. Berry, Y. Suzuki, A. Stebner, Manufacturing and flexural characterization of infusion-reacted thermoplastic wind turbine blade subcomponents, *App. Comp. Mater.* 3 (2019).
- [14] R.E. Murray, S. Jenne, D. Snowberg, D. Berry, D. Cousins, Techno-economic analysis of a megawatt-scale thermoplastic resin wind turbine blade, *Renew. Energy* 131 (2019) 111–119.
- [15] A. Le Duigou, P. Davies, C. Baley, Environmental impact analysis of the production of flax fibres to be used as composite material reinforcement, *J. Biobased Mater. Bioenergy* 5 (1) (2011) 153–165.
- [16] A. Chilali, W. Zouari, M. Assarar, H. Kebir, R. Ayad, Analysis of the mechanical behaviour of flax and glass fabrics-reinforced thermoplastic and thermoset resins, *J. Reinf. Plastics and Compos.* 35 (16) (2016) 1217–1232.
- [17] A. Chilali, W. Zouari, M. Assarar, H. Kebir, R. Ayad, Effect of water ageing on the load-unload cyclic behaviour of flax fibre-reinforced thermoplastic and thermosetting composites, *Compos. Struct.* 183 (January 2018) 309–319.
- [18] H.N. Dhakal, Z.Y. Zhang, M.O.W. Richardson, Effect of water absorption on the mechanical properties of hemp fibre reinforced unsaturated polyester composites, *Compos. Sci. Technol.* 67 (2007) 1674–1683.
- [19] A. Le Duigou, P. Davies, C. Baley, Seawater ageing of flax/poly(lactic acid) biocomposites, *Polym. Degrad. Stab.* 94 (7) (2009) 1151–1162. JulyPages.
- [20] D. Scida, M. Assarar, C. Poilâne, R. Ayad, Influence of hygrothermal ageing on the damage mechanisms of flax-fibre reinforced epoxy composite, *Compos. Part B: 48* (2013) 51–58.
- [21] A. Le Duigou, A. Bourmaud, P. Davies, C. Baley, Long term immersion in natural seawater of Flax/PLA biocomposite, *Ocean Eng.* 90 (2014) 140–148. NovPages.
- [22] A. Moudood, A. Rahman, A. Ochsner, M. Islam, G. Francucci, Flax fiber and its composites: an overview of water and moisture absorption impact on their performance, *J. Reinf. Plastics & Compos.* Vol. 38 (7) (2019) 323–339.
- [23] M. Le Gall, P. Davies, N. Martin, C. Baley, Recommended flax fibre density values for composite property predictions, *Ind. Crops & Prod.* 114 (2018) 52–58.
- [24] M. Bergès, R. Léger, V. Placet, V. Person, et al., Influence of moisture uptake on the static, cyclic and dynamic behaviour of unidirectional flax fibre-reinforced epoxy laminates, *Compos. Part A* 88 (2016) 165–177.
- [25] C. Kergariou, A. Le Duigou, et al., Measure of porosity in flax fibres reinforced poly(lactic acid) biocomposites, *Compos. Part A* 141 (2021), 106183.
- [26] F. Bensadoun, I. Verpoest, J. Baets, J. Muessig, N. Graupner, P. Davies, M. Gomina, A. Kervolen, C. Baley, Impregnated fibre bundle test for natural fibres used in composites, *J. Reinf. Plastics and Compos.* 36 (13) (2017) 942–957.
- [27] G. Coroller, et al., Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional composite, *Compos. Part A* 51 (2013) 62–70.
- [28] I. Straumit, D. Vendepitte, M. Wevers, S.V. Lomov, Identification of the flax fibre modulus based on an impregnated quasi-unidirectional fibre impregnated bundle test and X-ray computed tomography, *Comp. Sci. Tech.* 151 (2017) 124–130.
- [29] M.W. Tham, M.R. Nurul Fazita, et al., Tensile properties prediction of natural fibre composites using rule of mixtures: a review, *J. Reinf. Plastic & Comp.* 38 (5) (2019) 211–248.
- [30] H.B.H. Frej, R. Léger, D. Perrin, P. Janny, Effect of aging temperature on a thermoset-like acrylic thermoplastic composite for marine vessels, *J. Compos. Mater.* 55 (19) (2021), 002199832199678.
- [31] M.C. Symington, W.M. Banks, O.D. West, R.A. Pethrick, Tensile testing of cellulose based natural fibers for structural composite applications, *J. Comp. Mats Vol 43* (Issue 9) (2009) 1083–1108.
- [32] Arhant M., Davies P., Project Report, Realtide Deliverable D1.3, Test report Fatigue of composites for tidal turbine blades, 2019, <https://www.realtide.eu/sites/realtide.eng.ed.ac.uk/files/attachments/RLT-WP1-3-PDL-000-00-Test-report-Fatigue-of-composites-for-tidal-turbine-blades.pdf>.
- [33] M. Mehdikhani, L. Gorbatikh, I. Verpoest, S.V. Lomov, Voids in fiber-reinforced polymer composites: a review on their formation, characteristics, and effects on mechanical performance, *J. Comp. Mater.* 53 (12) (2019) 1579–1669.
- [34] Y. Li, Q. Li, H. Ma, The voids formation mechanisms and their effects on the mechanical properties of flax fiber reinforced epoxy composites, *Compos. Part A* 72 (2015) 40–48.
- [35] T. Cadu, M. Bergès, O. Scot, et al., What are the key parameters to produce a high-grade bio-based composite ? Application to flax/epoxy Ud laminates produced by thermocompression, *Compos. Part B: Eng.* 150 (2018) 36–46.
- [36] D.U. Shah, P.J. Schubel, M.J. Clifford, P. Licence, Fatigue life evaluation of aligned plant fibre composites through S-N curves and constant-life diagrams, *Compos. Sci. Technol.* 74 (2013) 139–149, <https://doi.org/10.1016/j.compscitech.2012.10.015>.
- [37] F. Bensadoun, K.A.M. Vallons, L.B. Lessard, I. Verpoest, A.W. Van Vuure, Fatigue behaviour assessment of flax-epoxy composites, *Compos. Part A* 82 (2016) 253–266.
- [38] S. Liang, P.-B. Birame, L. Guillamat, A comparative study of fatigue behaviour of flax/epoxy and glass/epoxy composites, *Compos. Sci. Technol. Elsevier* 72 (5) (2012) 535–543.
- [39] A. Stamboulis, C.A. Baillie, T. Peijs, Effects of environment on mechanical and physical properties of flax fibers, *Compos. Part A* 32 (2001) 1105–1115.
- [40] A. Thuault, S. Eve, D. Blond, J. Breard, M. Gomina, Effects of the hygrothermal environment on the mechanical properties of flax fibres, *J. Comp. Mater.* 48 (14) (2014) 1699–1707.
- [41] A. Celino, S. Fréour, F. Jacquemin, P. Casari, Characterization and modelling of the moisture diffusion behaviour of natural fibres, *J. Appl. Polymer Sci.* (2013) 1–10.
- [42] H.N. Dhakal, Z.Y. Zhang, N. Bennett, A. Lopez-Ariza, Vallejo, effects of water immersion ageing on the mechanical properties of flax and jute fibre biocomposites evaluated by nanoindentation and flexural testing, *J. Comp. Mater.* 48 (1) (2014) 1399–1406.
- [43] A. Malloum, A. El Mahi, Idriss, he effects of water ageing on the tensile static and fatigue behaviors of greenpoxy-flax fiber composites, *J. Comp. Mater.* 53 (21) (2019) 2927–2939.
- [44] M. Assarar, D. Scida, A. El Mahi, C. Poilane, R. Ayad, Influence of water ageing on mechanical properties and damage events of two fibre reinforced materials: flax-fibres and glass-fibres, *Mater. Des.* 32 (2011) 788–795.
- [45] C.H. Chen, G.S. Springer, Moisture absorption and desorption of composite materials, *J. Comp. Mater.* 10 (1976) 2–20.



- [46] D.S. Cousins, Advanced Thermoplastic Composites For Wind Turbine Blades, PhD thesis, Colorado School of Mines, 2018.
- [47] D.S. Cousins, Y. Suzuki, R.E. Murray, J.R. Samaniuk, A.P. Stebner, Recycling glass fiber thermoplastic composites from wind turbine blades, *J. Clean. Prod.* 209 (2019) 1252–1263.
- [48] H. Bel Haj Frej, R. Léger, D. Perrin, P. Jenny, P. Gérard, J.-F. Devaux, Recovery and reuse of carbon fibre and acrylic resin from thermoplastic composites used in marine application, *Resour. Conserv. Recycl.* 173 (2021), 105705.