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Flexural properties and failure mechanisms of infusible thermoplastic- and thermosetting based composite materials for marine applications



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ABSTRACT

This study aims to evaluate the flexural properties and associated failure mechanisms of a reactive thermoplastic relative to traditional thermosetting resin systems (polyester, vinylester, epoxy) for potential application in marine vessels over 50 m in length, as part of the H2020 FIBRESHIP project. All resin systems are compatible with the vacuum assisted liquid resin infusion manufacturing technique commonly used in small/medium size shipyards. Glass fibre reinforced polymer (GFRP) laminates were manufactured, test samples extracted, immersed in deionised water or an organic liquid (diesel) and mechanically tested to evaluate the flexural strength and modulus. Failure mechanisms are analysed by scanning electron microscope (SEM). In terms of flexural strength, the reactive thermoplastic based laminate performed similar to the epoxy in terms of retained strength in both deionised water and diesel. The governing failure mode of fibre buckling and kink band formation coupled with interlaminar cracking was identified for both the epoxy and the thermoplastic. The vinylester laminate retained equivalent strength in all three environments while polyester showed the greatest reduction in water due to extensive interlaminar cracking. Overall, the flexural properties of the reactive thermoplastic are shown to be competitive with traditional candidate resin systems for marine structures. The strength reduction and failure modes in the dry, wet and diesel condition were similar to the epoxy while the reduction of modulus was negligible in water and less than 10% in diesel.

1. Introduction

Glass fibre reinforced polymer (GFRP) composites currently dominate the manufacture of marine vessels up to 50 m in length, with liquid resin infusion (LRI) and vacuum-assisted liquid resin infusion in particular one of the most widely adopted manufacturing processes. The wide-scale adoption of GFRP composites into large marine structures has generally been hindered by the lack of qualification guidelines available from the classification societies. The current study is part of the FIBRESHIP Horizon 2020 funded EU project, which aims to further the use of FRP composites in the construction of marine vessels greater than 50 m in length by addressing this issue, in addition to tackling numerous other challenges associated with manufacturing large GFRP composite vessels [1–3].

During the service life of marine composites water uptake is inevitable and may cause plasticization, swelling, matrix hydrolysis or debonding of fibres from the matrix [4]. As a result, service life is shortened due to the degradation of mechanical and thermal proper-

ties and these factors must be evaluated when considering new materials for marine applications. Thermosetting resin systems are well established candidates for marine vessel applications due to a range of attributes including their compatibility with the resin infusion process in terms of low viscosity, the wide range of thermosetting chemistries available (e.g. epoxy, vinylester, polyester, phenolics) with an associated wide range of mechanical and environmental properties, competitive cost point and security of supply. However, the difficulties associated with disposing and/or recycling of large thermosetting based composite structures at the end of life has aroused increased interest in the use of thermoplastic based composites for large marine vessels. Reactive thermoplastics have an added benefit as they are compatible with the liquid resin infusion technique already widely used in ship yards, can be more readily repurposed at the end of life (formable under heat and pressure) or the constituents can be recycled [5] and have other benefits traditionally associated with thermoplastics such as the possibility of welding. Consequently, there is great potential for reactive thermoplastics to be applied in new marine

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applications and exploratory studies have recently been published in the open literature [6,7]. For example, Davies *et al.* evaluated the influence of seawater ageing on the mechanical behaviour of a reactive thermoplastic matrix (Elium from Arkema) which was reinforced with glass fibre [7]. Laminates were manufactured by vacuum assisted liquid resin infusion with a resulting fibre-volume-fraction of 0.52–0.58. The study focused on determining the moisture diffusion coefficient and tensile failure strength of cross ply (0/90°) and off-axis ($\pm 45^\circ$) laminates. The off-axis laminates exhibited strength retention of 92% after ageing in seawater at 60 °C for 18 months stabilising at approximately 1% moisture content. Drying after immersion did not provide full recovery of properties so at least one permanent damage mechanism occurred either at the fibre/matrix interface or the glass fibres themselves were compromised. SEM images of the $\pm 45^\circ$ specimens show cleaner fibres post aging suggesting damage of the fibre/matrix interface at least contributed to the reduction in strength [7]. Nash *et al.* evaluated the interlaminar shear strength (ILSS) of an acrylic based reactive thermoplastic (also Elium from Arkema) glass reinforced laminate and compared the results to laminates manufactured using traditional thermosetting resin systems (polyester, vinylester and epoxy). ILSS tests were performed in the dry condition and after immersion in deionised water (28 days, 35 °C) and diesel (7 days, 23 °C) [6]. Laminates were manufactured by liquid resin infusion in all cases with a resulting fibre-volume-fraction of 0.52–0.55. After immersion in deionised water, the thermoplastic laminate performed very well compared to the thermosetting based laminates in the dry condition but exhibited the largest reduction (-37%) in the wet condition. This was attributed to poor fibre–matrix interface adhesion as the failure was observed to transition from matrix-dominated cracking in the dry state to interfacial cracking after immersion. Despite the large reductions after immersion, the ILSS of the thermoplastic in the wet condition was still comparable to the vinylester and polyester based laminates. The thermoplastic also had the lowest uptake of diesel and retained 96% of its dry ILSS after 7 days of immersion - multiple short cracks were observed at failure in the diesel case.

At the time of writing, there are no other studies in the open literature focusing on the effect of environment (deionised, seawater, vehicle fluids) on the quasi-static mechanical properties of reactive thermoplastics and the associated failure mechanisms. Studies available in the open literature generally focus on thermosetting based glass fibre composites exposed to various liquid media such as water, oil, acids and alkalis. The following section reviews both the effect of water (seawater and deionised) and the effect of oils, acids and alkalis on mechanical properties and failure mechanisms.

Visco *et al.* (2008) evaluated the mechanical performance of two polyester (isophthalic and orthophthalic) based composites which were manually laid-up by hand [8]. It was concluded that the increased cost of isophthalics is justified due to the higher network density, which reduces water molecule diffusion, good fibre–matrix adhesion which produces superior mechanical and physical properties relative to the orthophthalic chemistry. The orthophthalic resin showed lower affinity with the glass fibre, generating voids and irregularities at the interface matrix/fibre. However, the reduction in flexural strength was similar for both materials (20%) after immersion in seawater (17 °C for 10 months) but the isophthalic based composite had a marginally lower reduction in modulus (13%) compared to the orthophthalic based composite.

In a follow on study, the effect of seawater on two glass–fibre reinforced composites (isophthalic polyester and vinyl ester) was reported [9]. Laminates were manufactured by the hand laminating technique with a resulting fibre-volume-fraction of 0.39 (polyester) and 0.32 (vinylester). The saturation levels for the polyester and vinylester were 1.2% and 0.71% respectively after immersion in seawater at 17 °C for 300 days. Regarding the polyester, there was a reduction in both flexural modulus (15%) and strength (20%) after immersion. The strength of the vinylester remained greater than 100% and the modulus actu-

ally increased steadily reaching approx. 120%. Experimental tests showed that vinylester has higher resistance to seawater absorption than isophthalic polyester due to the lower cure rate enabling it to organize its linear macromolecular chains in a more compact structure [9]. The tensile strength and interlaminar shear strength of unidirectional glass/epoxy laminates (manufactured by infusion) after exposure to natural seawater and deionised water were investigated by Dawson *et al.* [10]. The tensile strength of samples exposed to seawater and deionized water (eight months at 40 °C) decreased by approximately 28 and 34% respectively compared to unaged composites while the ILSS decreased by 25 and 31% respectively. Ageing in deionised water slightly decreased the time required to achieve a given level of saturation, but it also clearly had a greater adverse effect on the mechanical performance compared to ageing in natural seawater.

Xu *et al.* studied the residual compressive properties of E-glass/vinylester composite after exposure to seawater for 29 months [11]. Plain woven GFRP composites were manufactured by vacuum assisted liquid resin infusion resulting in a fibre-volume-fraction of 0.54. The composite samples were then subjected to impact damage followed by residual compressive strength analysis after only one side of the laminates was exposed to seawater representative of the exposure experienced by the hull of a marine vessel in service. The results revealed a 10% reduction in compression strength for seawater exposed impact damaged samples compared to the dry baseline samples. SEM images confirmed a reduction in fibre–matrix interfacial adhesion after exposure to seawater with delamination caused by sub-laminate buckling being the main failure mode.

The effect of hygrothermal ageing (95% relative humidity at up to 70 °C using a climatic chamber) on the interlaminar shear strength (ILSS) of glass reinforced epoxy composites manufactured by wet lay-up was evaluated and a reduction of approximately 36% was reported after 260 h of exposure [12]. It was concluded that it is not only the absorbed moisture but also the diffusion conditions that affect the interfacial degradation phenomena. SEM analysis highlighted both interfacial cracking and de-adherence of the matrix from the fibres in aged ILSS samples.

Mittal *et al.* studied the influence of seawater on the flexural behaviour of MMT (montmorillonite) clay based glass fiber/vinylester composites manufactured by hand layup coupled with hot press moulding [13]. The flexural strength of control (untreated MMT) and MMT clay (treated with a silane-based coupling agent) decreased by 7 and 4.5% respectively compared to dry samples after immersion in seawater for 65 days. SEM images of the failed samples showed that the reduction was caused by the swelling of MMT after seawater absorption, which resulted in deterioration of the adhesion and interactions between the MMT and the matrix. Change in flexural modulus due to seawater absorption was negligible for both cases.

The failure mechanisms associated with a basalt reinforced epoxy tested in flexure after exposure to deionised water (35 °C) until fully saturated were reported by Chowdhury *et al.* [14]. A 19% reduction in flexural strength and a negligible change in modulus was reported. For both dry and moisture-aged specimens, similar failure modes were observed by SEM on the compression side (fibre kinking on 0° fibres, inter-ply and intra-ply delamination) and on the tension side (fibre breakage in 0° fibres, inter-ply delamination and transverse shear crack in 90° tows). On the compression side, the dry specimen exhibited damage at 50% of peak stress while damage occurred in the moisture-aged specimens somewhere between 50 and 80% of failure. On the tension side, evidence of damage was only evident at failure for the dry specimens. However, extensive damage was evident on the tension side at 80% of peak stress for the moisture-aged specimens. Overall, it was clear that damage occurs on the compression side first and that fibre buckling and kinking dominate the failure process.

Stamenovic *et al.* studied the tensile properties of glass reinforced polyester composite pipe manufactured by filament winding after exposure to a range of solutions including a strong acid (pH1), a strong

base (pH14) and pure water (pH7) for periods of 3–60 days [15]. In all cases, changes to the modulus were less than half the change in strength. For water, a reduction in tensile strength (-16%) and modulus (-4%) was reported after 60 days. Greater reductions in strength (-26%) and modulus (-8%) were reported after 60 days exposure to the strong base. Weakening of fibre–matrix connectivity was cited as the main factor governing the response to both solutions.

The effect of different acid solutions (HCl and H₂SO₄) on the flexural properties of glass reinforced epoxy composites manufactured using an autoclave was studied by Amaro *et al.* [16]. In contrast to the results reported by Stemenovic *et al.* [15] who reported an increase in tensile strength (+12%) and tensile modulus (+6%) after exposing glass reinforced polyester to a strong acid for a 60 day period, a significant reduction in flexural strength (16%) and modulus (22%) were reported after exposure to an acidic solution (HCl) for 36 days. In order to explain the reductions, complimentary tests including absorption measurements, SEM analysis of surface morphology, roughness and hardness measurements were performed. The SEM images revealed that contact with acid solution promoted micro cracking and surface roughness also increased. Hardness measurements revealed that ageing caused a reduction in Young's modulus. Consistent with Stemenovic *et al.* an alkaline solution caused reductions in both flexural strength (22%) and modulus (27%) after 36 days of exposure time [17]. Regarding the failure mechanisms of all laminates, the main damage observed occurred initially by fibre fracture on the tensile surface followed by inter-ply delamination. Independently of the solution used, delamination size increased with the duration of immersion and was always higher for alkaline solutions compared to the acid solutions.

The effect of different commercial oils on the mechanical properties of glass/epoxy composites produced by an autoclave/vacuum-bag moulding process was also studied by Amaro *et al.* [18]. The flexural strength of the laminate samples exposed to engine oil (15 W-40) and brake fluid (DOT 4) was reduced by 7 and 11%, respectively, after 45 days of exposure. Failure started on the tensile surface in all three cases followed by compression failure of fibres under the loading pin. Both solutions caused delamination on the tension side. However, samples exposed to Dot 4 also showed extensive cracking at mid-thickness. It was concluded that the solutions promote matrix-fibre interface degradation.

Condruz *et al.* performed tensile tests on composites aged with kerosene and saline solutions [19]. Two types of carbon fibre based prepreg (epoxy and epoxy/cyanate ester) were used to manufacture laminates by autoclave. Both materials showed a weight gain of 0.10% after the first 7 days of immersion in kerosene and 0.16% after the 73 days of immersion in kerosene. The weight gain of both composites in saline solution was slightly lower at 0.13% after 7 days of immersion. Overall, the results showed that kerosene and saline solution had no influence on the elastic modulus of the materials, but did cause a slight increase in tensile strength (3–5%). Peeling, cracking or matrix dissolution of the polymer composites was not observed after immersion in either saline solution or kerosene.

Overall, the majority of the aging studies reviewed consider thermosetting based GFRP composites which have limited potential in terms of achieving a circular economy through recycling at the end of life. Consideration of materials with increased potential for recycling or repurposing at the end of life is a pressing societal issue globally due to climate change and evolving environmental legislation. However, only two studies have focused on infusible reactive thermoplastics which are promising new candidates for application in the marine sector [6,7]. It is also generally clear from the literature that significant changes in the mechanical properties can be expected after aging of composites in both water and more aggressive media but more studies are required to provide evidence to help explain and understand the controlling failure mechanisms.

The aim of the current study is to evaluate the flexural properties of an infusible reactive thermoplastic matrix system (Elium from Arkema) relative to thermosetting matrices most commonly used in

marine structures after exposure to water and an organic liquid (diesel) and to improve understanding of the associated failure modes. Flexural properties (strength and modulus) are of main interest as the bending resistance of laminates used in the construction of the hull and main girders is critical in the design of large composite marine vessels to ensure strength and serviceability limits are not exceeded. The interlaminar shear properties have already been reported [6]. Commercially available vinylester, polyester and epoxy resin systems and an infusible reactive thermoplastic were used to manufacture GFRP laminates using vacuum assisted liquid resin infusion. The flexural strength and flexural modulus of specimens tested under dry conditions and after an immersion period in deionised water and diesel were evaluated and the failure mechanisms analysed by SEM.

2. Materials and methods

2.1. Materials

The following polymer matrices were used in the current study:

- EP: Epoxy - PRIME™ 27 from Gurit
- VE: Vinylester - LEO Injection Resin 8500 from BÜFA (this resin is part of the Saertex LEO® fire retardant composite system)
- PE: Dicyclopentadiene-based Polyester - Synolite 8488-G2 from Aliancys
- TP: Thermoplastic – Elium® 150 from Arkema

The properties and curing details of all matrices are summarized in Table 1. The reinforcement fabrics used were SAERTEX U-E-996 g/m² unidirectional (UD) non-crimp glass fabric and SAERTEX U-E-940 g/m²-LEO UD non-crimp glass fabric. The LEO UD fabric was used only with the LEO VE resin, as part of the LEO® composite system. Regarding the reinforcement fabric, 90% of the glass fibres are in the axial (0°) direction and 10% are in the transverse (90°) direction. The latter help to stabilise the fibre architecture prior to infusion.

2.2. Laminate manufacture

A [0°]_{2S} stacking sequence was used to produce all laminates using the vacuum assisted liquid resin infusion technique. This approach has been designated RIFT II in the literature [20] and is normally used for the manufacture of marine vessel components. All laminates were manufactured by placing the dry reinforcement fabric, peel ply and flow medium on a glass tool. The lay-up was then enclosed beneath a flexible membrane secured to a glass tool using sealant tape. The processing conditions (ratios of curing agent, curing and post-curing) were followed as shown in Table 1. All resin systems were infused without prior degassing at ambient temperature (approximately 20 °C). A vacuum pump was used to obtain a pressure in the range 10–20 mbar (absolute) inside the vacuum bag. Monomer boiling was not observed for any of the resin systems considered in this study. The ambient temperature (20° C) and infusion time (~20 min.) were approximately the same for each infusion. A water-cooled diamond-coated rotating disc cutter was used to extract the test coupons from the laminates.

2.3. Environmental conditioning

Pre-drying of all coupons was performed for four hours at 45 °C before testing. Flexural testing was performed on dry samples after pre-drying. Wet conditioned sample were immersed in deionised water at 35 °C for 28 days in accordance with Lloyds Register Book K, Procedure 14–1, Rev 1 Dec 2013. Standard grade road diesel fuel was used to immerse the organic-wet condition samples over a period of seven days. Deionised water was selected for conditioning the test samples in this study as it is generally considered to have a greater detri-

Table 1
Cured resin properties according to manufacturer datasheets.

Description	EP	VE	PE	TP
Name	Prime 27	Leo-M-8500	Synolite 8488-G	Elium 150
Curing Agent	Prime 20 Slow Hardener	Butanox M – 50	Butanox M – 50	Perkadox CH-50X
Mass Ratio (Resin : Curing Agent)	100 : 28	100 : 2.5	100 : 1.5	100 : 2.5
Density	1.08 g/cm ³	1.04 g/cm ³	1.05 g/cm ³	1.19 g/cm ³
Viscosity	190–200 mPa.s @25 °C	300–400 mPa.s @20 °C	80–90 mPa.s @23 °C	100 mPa.s @25 °C
Gel Time	2hr 40 min @25 °C	1hr 50 min @20 °C	1hr 30 min @23 °C	25 min @25 °C
Curing time at ambient	24 hr	24 hr	24 hr	24 hr
Post-cure temperature	60 °C	80 °C	40 °C	Not required
Post-cure time	7 hrs	6 hrs	16 hrs	Not required
Heat deflection temperature	60–62 °C	105 °C	64 °C	109 °C

mental effect on mechanical properties such as tensile strength and inter-laminar shear strength compared to sea water [21,22]. Dry mass and soaked mass were calculated for wet and organic-wet conditions samples after pre-drying and after soaking in the respective liquids.

2.4. Fibre volume fraction (v_f)

Fibre volume fraction for each laminate was determined using thickness measurements in accordance with ISO 14127. Cured ply thickness is also reported based on thickness measurements of the [0°]_{2S} laminates.

2.5. Three-point bend flexure experimental procedure

Three-point bend tests were performed under quasi-static loading conditions in accordance with ISO 14125. Nominal specimen dimensions were 100 mm × 15 mm × 3 mm. A nominal span length of 60 mm was used, at a testing speed of 1 mm/min. The upper roller diameter was 10 mm and the diameter of the lower rollers was 4 mm. Five samples were tested for each condition. Flexural modulus was measured between 0.0005 and 0.0025 strain.

2.6. Scanning electron microscopy (SEM)

Cross-sections of tested three-point bend specimens from all conditions (dry, wet, organic-wet) were studied using a Hitachi SU-70 SEM at a voltage of 10 kV and a working distance of 10 mm. Specimens were mounted in a two-part epoxy (Epoxicure Resin and Epoxicure Hardener in a ratio of 5:1) with a conductive powder filler and polished prior to SEM observation. SEM images of the centre of each flexural test samples were captured. All images were captured at the same magnification so that the features and evidence of damage are comparable in terms of scale.

3. Results and discussion

3.1. Environmental conditioning and physical properties

The results of the physical tests are summarised in Table 2. Laminates showed similar cured ply thickness, and similar v_f in the range of 0.52–0.55. As a result of the similar v_f values, the amount of water absorbed by the samples can be compared directly. Higher v_f may lower the water uptake potential of laminates because the water diffusion path is hindered by the fibres and consequently the diffusion rate

Table 2
Cured ply thickness, fibre volume fraction, average water uptake and average diesel fuel uptake values of each material tested.

Material	Cured Ply Thickness	v_f	Average Water Uptake (28 days, 35 °C)	Average Diesel Fuel Uptake (7 days, 23 °C)
VE	0.71 mm	0.52	0.23% ± 0.02%	0.07% ± 0.02%
PE	0.73 mm	0.54	0.28% ± 0.02%	–0.03% ± 0.02%
EP	0.74 mm	0.53	0.47% ± 0.02%	0.07% ± 0.03%
TP	0.72 mm	0.55	0.42% ± 0.02%	0.09% ± 0.04%

of the water molecules is slower [23]. The results of water and diesel fuel uptake for flexure test specimens after immersion are also summarised in Table 2. Each specimen was weighed before and after immersion to determine the amount of liquid uptake, which is expressed as a percentage of the dry specimen mass. It is worth noting at this point that the moisture uptake presented here is just a snapshot of the diffusion of moisture into the specimens. The purpose of this test was to evaluate the performance of the materials after the immersion conditions stated by the marine classification society Lloyds Register Book K, Procedure 14–1, Rev 1 Dec 2013. These values are not indicative of the maximum equilibrium moisture content, nor of the diffusivity mechanisms present in the specimens. Diffusion kinetics of the liquid into the specimen was not studied as part of this work.

The VE specimens showed the lowest water uptake (0.23%) of all materials studied. This could be potentially attributed to the bespoke sizing on the glass fibres in the VE (LEO system) fabric. Similar observations were made for carbon fibre/epoxy composites [24], where specimens with a bespoke sizing absorbed less water compared to unsized counterparts. PE exhibited the second lowest water uptake, which could be attributed to the highly hydrophobic nature of the dicyclopentadiene-based PE matrix. With respect to EP and TP, the water uptake for the EP specimens was 11% higher than that of the TP specimens, which follows a similar trend to other studies [25,26].

The uptake of diesel fuel was low across all specimens (partly due to the short immersion time). The PE system actually showed a slight reduction in mass for each sample weighed. The PE resin used in this study is a dicyclopentadiene-based (DCPD) unsaturated polyester. These polyesters are generally known to reach lower molecular weight values compared to other polyesters (isophthalic, orthophthalic) and vinyl esters, as they use less styrene (DCPD improves solubility of the polyester resin in styrene, so less styrene is used) [27]. Lower styrene content and lower post-cure temperature for the PE compared to the VE resin (40 vs 60 °C, respectively - see Table 1) can lead to a cross-linked network of lower cross-linking density with a relatively high soluble fraction after curing. This soluble fraction could have been at least partly dissolved in the diesel fuel during immersion (DCPD and diesel are both hydrocarbon-based) and this may explain the observed mass loss for PE.

3.2. Flexural Strength, modulus and failure modes

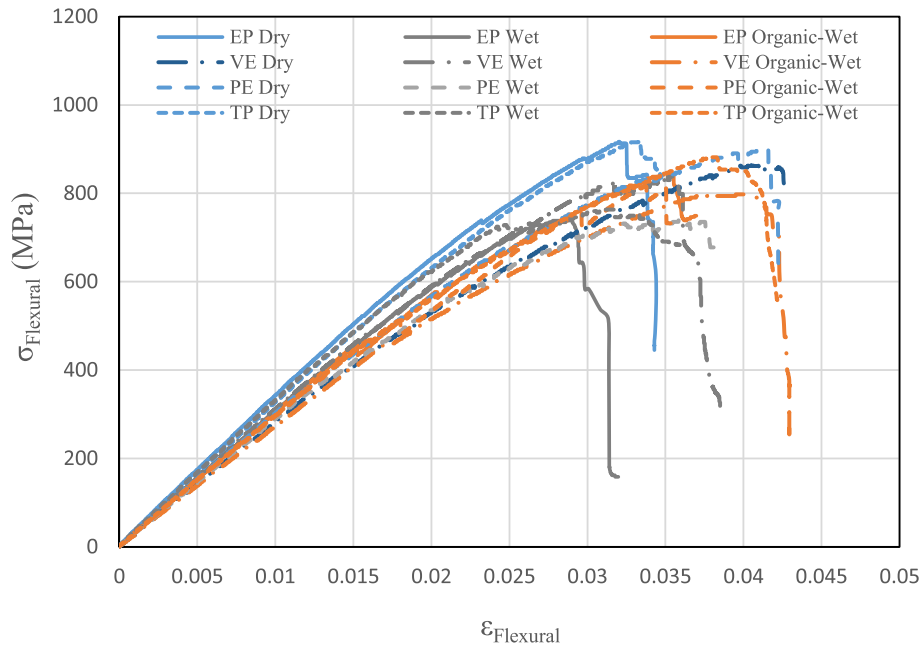
The flexural strength, modulus and strain at failure for all materials under dry, wet and organic-wet conditions are shown in Fig. 1 and in tables 3, 4 and 5.

The dry flexural strength of the TP, EP and PE are comparable (in the range of 916–942 MPa), and the effects of conditioning in both liquids are similar for each of the three materials as shown in Table 3. Water reduces the flexural strength by 19%, 23% and 17% for EP, PE and TP, respectively, while diesel reduces the flexural strength by 8%, 3% and 5% for EP, PE and TP, respectively.

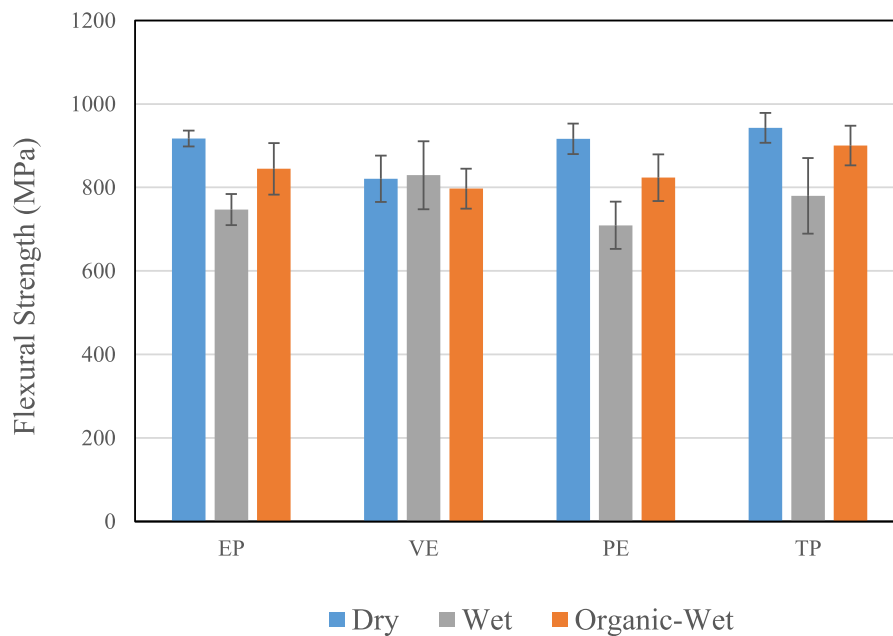
The VE system had the lowest dry flexural strength, which may partly be due to the marginally lower areal weight (5%) of the reinforcement used with the VE. However, VE showed consistent resis-

tance to the effects of water (+1%) and diesel (-3%) in terms of flexural properties. In terms of strain at failure, water immersion caused a reduction in all materials of 10–18%, while the effect of diesel was mixed. Strain at failure increased for both EP and TP (12–16%), remained approximately the same for VE and decreased for PE (-10%).

TP laminates exhibited the second highest flexural strength retention for water and diesel aged samples (83 and 95%, respectively). All TP laminates exhibited buckling under flexural load on the com-

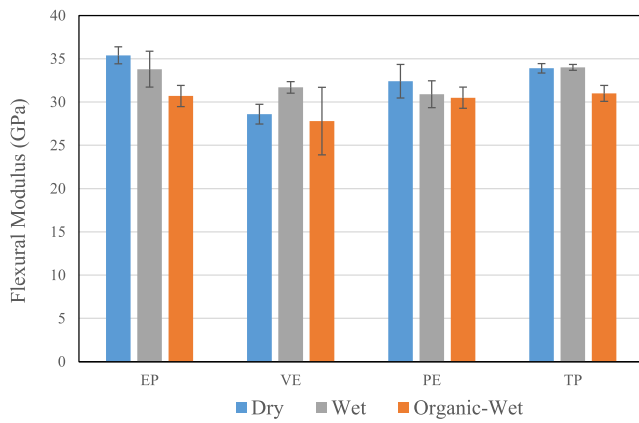


(i)

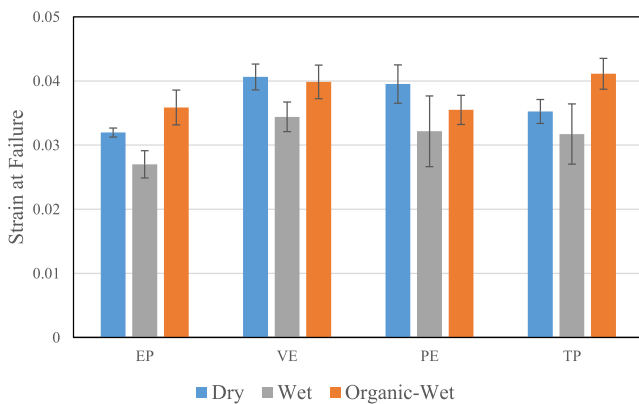


(ii)

Fig. 1. Summary of the results for each material system under dry, wet and organic-wet conditions: (i) flexural stress/strain curves (ii) flexural strength (iii) flexural modulus (iv) strain at failure.



(iii)



(iv)

Fig. 1 (continued)

pression side, which was confined, to the first layer (0°) as shown in Fig. 2. The observed failure mode was consistent in all three cases, consisting of fibre buckling followed by fibre breakage. There was also a hint of interlaminar failure between the first and second ply after diesel ageing. The modulus was negligibly affected by water but strain at failure reduced by 10% due to failure occurring earlier at 83% of the dry case. However, diesel caused a reduction of the modulus by 8.6% and a corresponding increase in strain at failure (+16%) – the interlaminar cracking noted earlier may have played a role here. The wet case shows a resin rich region in the second ply (from top) and on closer inspection, polyester stitching is visible within the resin rich

Table 3
Flexural Strength for EP, VE, PET and TP composite laminates.

Material	Flexural Strength (MPa)		
	Dry	Wet*	Organic-Wet*
EP	917.1 ± 18.7	746.7 ± 37.34 (-18.6%)	844.6 ± 61.66 (-8.0%)
VE	820.7 ± 55.8	829.2 ± 81.27 (+1.0%)	797.3 ± 47.83 (-3.0%)
PE	916.2 ± 36.6	709.29 ± 56.74 (-22.6%)	823.3 ± 55.98 (-10%)
TP	942.8 ± 35.8	779.8 ± 90.46 (-17.3%)	900.3 ± 47.71 (-5.0%)

* The change in these properties relative to the “dry” values due to the presence of fluid in the wet and organic-wet specimens is shown below the “wet” and “organic-wet” value in parentheses.

Table 4
Flexural modulus for EP, VE, PET and TP composite laminates.

Material	Flexural Modulus (GPa)		
	Dry	Wet*	Organic-Wet*
EP	35.4 ± 1.0	33.8 ± 2.0(-4.5%)	30.7 ± 1.2(-13.3%)
VE	28.6 ± 1.1	31.7 ± 0.7(+10.8%)	27.8 ± 3.9(-2.8%)
PE	32.4 ± 1.9	30.9 ± 1.5(-4.6%)	30.5 ± 1.2(-5.9%)
TP	33.9 ± 0.5	34.0 ± 0.3(+0.3%)	31.0 ± 0.9(-8.6%)

* The change in these properties relative to the “dry” values due to the presence of fluid in the wet and organic-wet specimens is shown beside the “wet” and “organic-wet” value in parentheses.

region. In this case, the cutting plane has passed directly between two 0° fibre tows. At this location the polyester stitching required to stabilise the fibre tows creates a gap which is occupied by the resin and the polyester stitching.

The epoxy retained 81 and 92% of its flexural strength after immersion in water and diesel, respectively (Table 3). In the dry and organic-wet condition, failure occurred in the first ply of 0° fibres on the compression side under the load nose (Fig. 3). The fibres have buckled in both cases and a kink band is clearly evident in the dry state. An interlaminar crack is also evident between the first and second plies in both cases. In the wet case, it is clear that the fibres have also buckled in the second ply as well as the first ply, which may explain why the level of retention was only 81%. There also appears to be an interlaminar crack at the bottom of the second ply. In water, the reduction in modulus was greater than TP (-4.5%) and exhibited a higher variance. The reduction in strain at failure of the EP (-15%) was greater than TP (-10%) due to the combined effect of the reduction in modulus and the reduction in strength. In diesel, the reduction in modulus was also greater than TP (-13.3%) but the corresponding increase in strain at failure was marginally less (+12%) than TP (+16%).

VE retained 101% and 97% of its flexural strength after immersion in water and diesel respectively showing that water and diesel had little effect on the strength after the immersion periods considered in this study. However, the failure mechanism is not consistent across the three different cases. Fibre buckling is most clear in the dry condition and damage is confined to the first ply under the load nose (Fig. 4). While there is evidence of fibre buckling for the wet and organic-wet cases, the damage is not localised and extends much further along the zero degree fibres unlike in the dry case. The modulus actually increased in water (+10.8%) with a corresponding decrease in strain at failure (-15%). In diesel, the modulus and strain at failure of VE were only marginally affected (-2.8% and -1.9% respectively).

PE retained 77 and 90% of its flexural strength after ageing in water and diesel, respectively. Buckling in the first ply is clearly evident in both the wet and diesel cases and is confined to the first ply

Table 5
Strain at failure for EP, VE, PET and TP composite laminates.

Material	Strain-at-Failure		
	Dry	Wet*	Organic-Wet*
EP	0.032 ± 0.007	0.027 ± 0.002 (-15.6%)	0.036 ± 0.003 (+12.2%)
VE	0.041 ± 0.002	0.034 ± 0.002 (-15.3%)	0.040 ± 0.003(-1.9%)
PE	0.0395 ± 0.003	0.032 ± 0.006 (-18.6%)	0.035 ± 0.002 (-10.2%)
TP	0.0353 ± 0.002	0.032 ± 0.005 (-10.0%)	0.041 ± 0.002 (+16.7%)

* The change in these properties relative to the “dry” values due to the presence of fluid in the wet and organic-wet specimens is shown beside the “wet” and “organic-wet” value in parentheses.

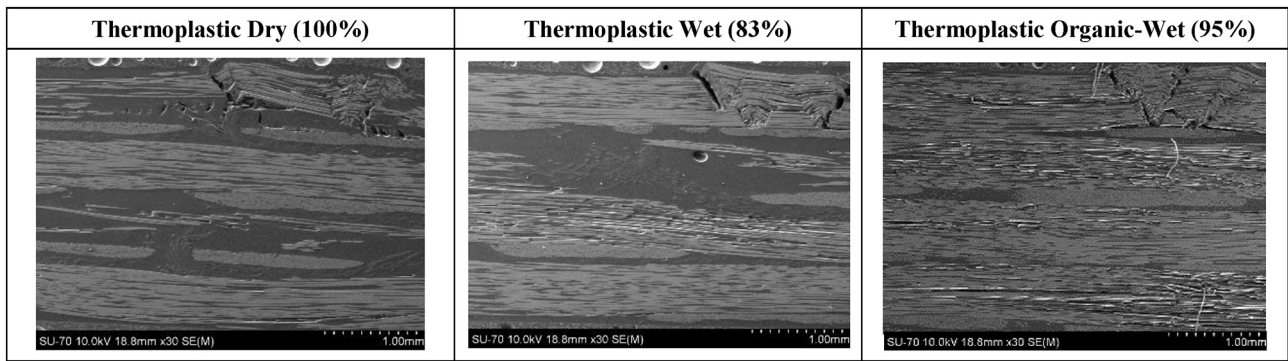


Fig. 2. SEM images of tested thermoplastic flexural specimens under dry, wet and organic wet conditions. The percentage failure strength is also shown relative to the dry condition.

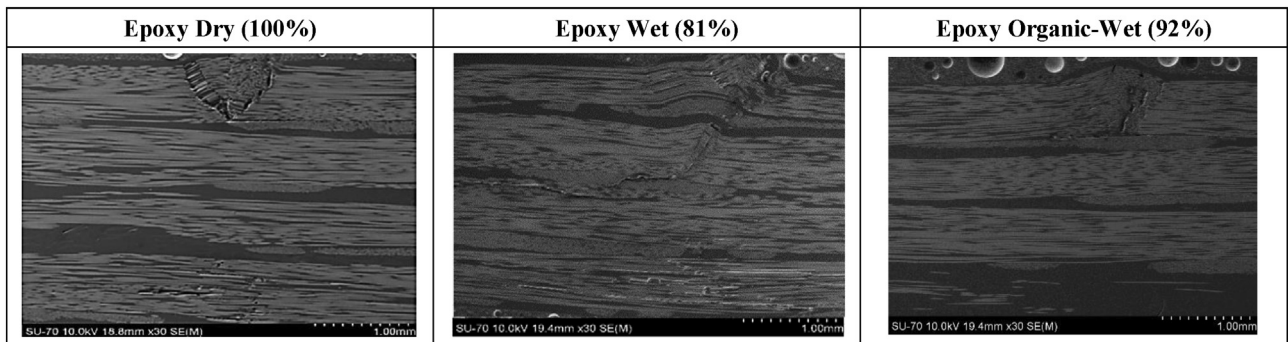


Fig. 3. SEM images of tested epoxy flexural specimens under dry, wet and organic wet conditions. The percentage failure strength is also shown relative to the dry condition.

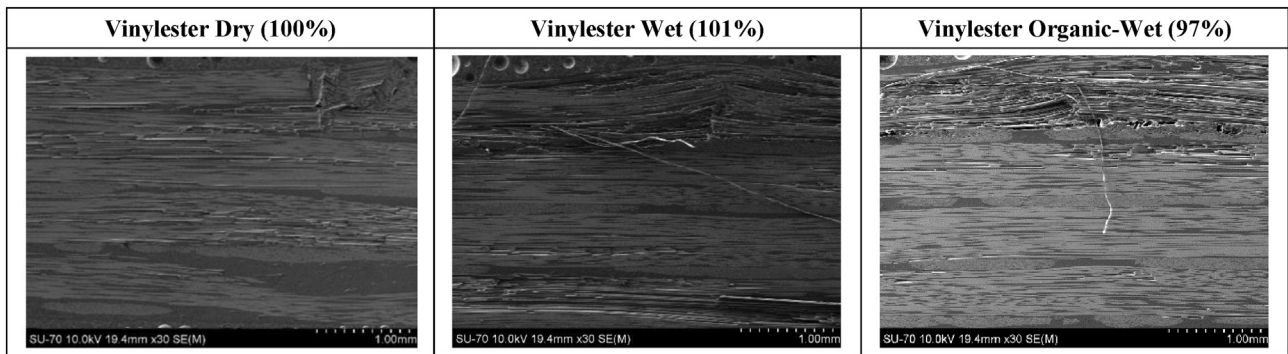


Fig. 4. SEM images of tested vinylester flexural specimens under dry, wet and organic wet conditions. The percentage failure strength is also shown relative to the dry condition.

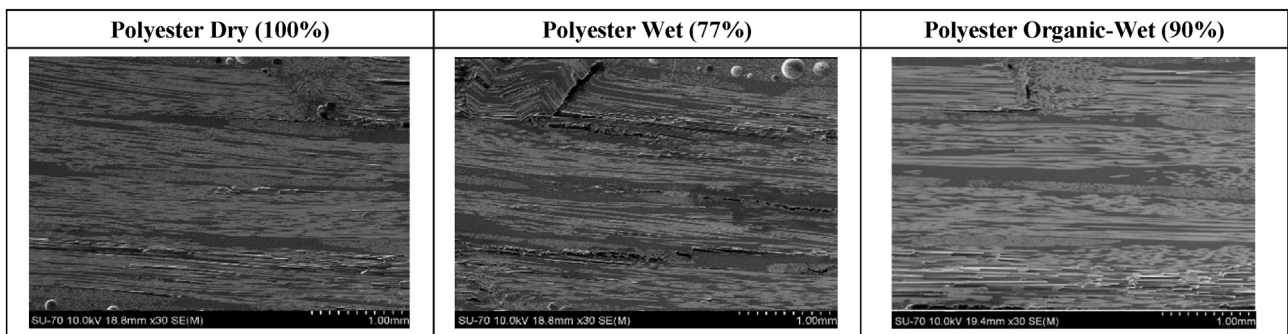


Fig. 5. SEM images of tested polyester flexural specimens under dry, wet and organic wet conditions. The percentage failure strength is also shown relative to the dry condition.

(Fig. 5). The wet case shows interlaminar cracking between all four plies, which may be responsible for the significant drop in strength (-23%) while the diesel case only exhibits an interlaminar crack between the first and second ply which also correlates with the drop in strength measured (-10%). The effect of environment on strength is more critical for the PE as the reduction in elastic modulus was only 4.6% in water and 5.9% in diesel. However, strain at failure was also significantly reduced in both water (-18%) and diesel (-10%) compared to the dry case

4. Limitations and future scope of current work

While the current study is focused on the effect of deionised water and diesel on the flexural properties of an infusible thermoplastic matrix/glass fiber reinforced composite material and its comparison with traditional candidate resin systems for marine applications, it is of course important to evaluate other properties which are central to the successful application of the material in a marine environment. For example, a study on the interlaminar strength which is a good indicator of fibre/matrix bond strength has already been completed [6]. In addition, composites in marine applications are subjected to repeated cyclic loading, causing fatigue damage within the structure and the fatigue mechanisms involved are generally not very well understood and difficult to predict. Work on the fatigue performance of this material has also been conducted and will be published in the near future.

5. Conclusion

Reactive thermoplastics are promising candidate materials for large length composite marine vessels due to attractive attributes such as compatibility with the liquid resin infusion manufacturing processes currently used in shipyards and they also possess greater potential for repurposing/recycling at the end of life compared to thermosetting resin systems. This study focuses on evaluating the effect of deionised water and diesel on the flexural properties of a reactive thermoplastic (TP) resin system compared to three other more traditional thermosetting candidates i.e. vinyl ester (VE), polyester (PE) and epoxy (EP). The flexural strength of each laminate and the associated failure modes are analysed for each environmental condition and the flexural modulus is also presented to address the serviceability aspect. Flexural strength and modulus were evaluated under dry conditions and after a period of immersion in deionised water (28 days, 35 °C) and a relevant organic liquid (diesel fuel, 7 days, 23 °C). The key findings of this study are:

- The manufactured laminates exhibited similar cured ply thickness and fibre-volume-fraction values, the latter in the range of 0.52–0.55. TP absorbed 11% less moisture than EP but 33% more than PE and 45% more than VE. Diesel fuel uptake was highest for TP (0.9%) with EP and VE showing similar but slightly lower levels of uptake (0.7%).
- In the dry condition, the failure mode is reasonably consistent for the four different laminates i.e. fibre buckling and kink band formation on the compression side under the load nose. TP exhibited the highest flexural strength (942 MPa), while EP and PE exhibited marginally lower flexural strengths relative to TP. EP exhibited the highest modulus followed by TP. VE exhibited the lowest flexural strength (820 MPa) and modulus.
- Regarding immersion in deionised water, TP exhibited the lowest reduction in flexural strength (-17%) and a negligible change in modulus (+0.3%). Fibre buckling was confined to the first ply under the load nose and interlaminar cracking was not observed. The flexural strength of EP and PE decreased by 19% and 23% respectively while reduction in modulus was less than 5% for both.

The epoxy exhibited fibre buckling in both the first and second plies under the load nose and interlaminar cracking between the second and third ply. Interlaminar cracking was evident between all four plies of PE. VE showed a negligible change in flexural strength (+1%) but the failure mode was significantly different to the dry case. Also, the damage was not localised under the load nose and actually extended much further along the zero degree fibres unlike in the dry case.

- Regarding immersion in diesel, TP showed a 5% reduction in strength whereas EP and PE showed reductions of 8% and 10%, respectively. The failure mode in TP was fibre buckling confined to the first ply and interlaminar cracking between the first and second ply. The failure mode in the EP and PE was very similar to TP. Regarding VE, reduction in strength was lowest (3%) and the failure mode was significantly different to the others and most similar to VE in the wet case. Reduction in flexural modulus was maximum for EP (13%) while TP exhibited the second highest reduction of 8.6%.

Overall, this study shows that the flexural properties of the reactive thermoplastic are competitive with traditional candidate resin systems for marine structures under the conditions investigated in this study. The strength reduction and failure modes in the dry, wet and diesel condition were similar to the epoxy while the reduction of modulus was negligible in water and less than 10% in diesel. A comprehensive testing and qualification programme including fire resistance would of course be required before any wider endorsement and adoption of any of the material systems considered in this study.

Author declaration/Conflict of interest

The authors do not have any conflicting financial or other interests. This study was conducted using composite laminates manufactured at the University of Limerick, and focussed on a specific range of their properties. It does not constitute a complete or universal assessment of the constituent materials used to manufacture the composite laminates (resin systems and glass fibre fabrics) and therefore makes no related claims on suitability, preference, ranking, or any endorsement whatsoever in a commercial context. Manufacturer and/or end-user requirements should be considered carefully in each individual case for material selection purposes.

CRediT authorship contribution statement

T. Gobikannan: Writing - original draft, Investigation, Formal analysis. **A. Portela:** Investigation, Formal analysis. **A.K. Haldar:** Writing - review & editing, Visualization. **N.H. Nash:** Investigation, Formal analysis, Writing - original draft. **C. Bachour:** Investigation, Formal analysis. **I. Manolakis:** Conceptualization, Methodology, Writing - review & editing, Funding acquisition, Project administration. **A. J. Comer:** Supervision, Conceptualization, Visualization, Methodology, Writing - review & editing, Methodology, Supervision, Funding acquisition, Project administration.

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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Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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