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Effect of environmental conditioning on the properties of thermosetting- and thermoplastic-matrix composite materials by resin infusion for marine applications

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ABSTRACT

Glass-fibre reinforced polymer (GFRP) laminates were manufactured using Vacuum assisted Resin Transfer Moulding (VaRTM) with a range of thermosetting resins and an infusible thermoplastic resin as part of a comprehensive down-selection to identify suitable commercially available resin systems for the manufacture of marine vessels greater than 50 m in length. The effect of immersion in deionised water and in an organic liquid (diesel) on the interlaminar shear strength (ILSS) and glass transition temperature (T_g) was determined. The thermoplastic had the highest T_g of all materials tested and comparable ILSS properties to the epoxy. Immersion in water, however, caused larger reductions in ILSS properties of the thermoplastic compared to the other systems. SEM showed a transition from matrix-dominated failure in the dry condition to failure at the fibre-matrix interface in the wet and organic-wet specimens. The overall performance of the infusible thermoplastic is good when compared to well-established marine resin systems; however, the environmental performance could be improved if the thermoplastic resin is used in conjunction with a fibre sizing that is tailored for use with acrylic-based resin systems.

1. Introduction

Glass-fibre reinforced polymer (GFRP) composite materials are the most widely adopted amongst fibre-reinforced polymer (FRP) composites globally, with approximately 1 million tons produced annually in the EU alone [1]. GFRP composite materials have excellent balance between good performance (i.e. high specific stiffness and strength) and low cost, compared to FRP utilising other commercially available fibres (e.g. carbon, aramid). As a result, GFRP composites are currently dominating the manufacture of marine vessels up to 50 m in length, with liquid resin infusion (LRI) being the most frequently used manufacturing technique and vacuum-assisted resin transfer moulding (VaRTM) in particular the most widely adopted LRI variant. The wide-scale adoption of FRP composites into large marine structures is often hindered by the lack of guidelines available for qualification of these materials by classification societies. This work 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 FRP composite ships.

The main benefits of GFRP in shipbuilding include: significant weight reduction resulting in substantial fuel saving and reduced greenhouse gas emissions, increase in cargo capacity, improved life-cycle performance and reduced maintenance costs due to improved corrosion resistance. Despite the many benefits associated with the use of GFRP, the increasing amount and handling of end-of-life composite parts has a negative impact on the environment [2]. As a result, current environmental legislations in relation to future waste management require all engineering materials to be properly recovered and recycled from end-of-life products and vehicles [3,4]. However, the current potential for recycling marine composites (typically glass fibre reinforced polyester, vinylester or epoxy thermoset matrix) is limited. Rybicka et al. [5] analysed the technology readiness level (TRL) of many composite recycling techniques, and found that environmentally harmful techniques, such as incineration and landfilling, and techniques with high-energy requirements, such as pyrolysis for carbon fibre and mechanical grinding for glass fibre, are currently the only recovery and disposal techniques with high TRL levels.

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Thermoplastic matrix composite components can be reformed or reshaped using heat and/or pressure and therefore offer the potential for recycling end-of-life composite structures. They also offer improved fracture toughness over thermosets, as well as the ability to be easily joined using welding techniques. Otheguy et al. [6] demonstrated that a thermoplastic-based composite hull of a rigid inflatable boat (made from a composite sandwich structure composed of glass/polypropylene laminate, balsa core material and paint) could be recycled by melt processing into injection mouldable granules that have acceptable properties when processed. However, as shipyards primarily use resin infusion manufacturing techniques for composite hulls, most thermoplastic matrix materials are not suitable due to their high melt temperatures and viscosities. Arkema have developed an acrylate-based thermoplastic liquid resin family (Elium®) that can be used for room-temperature resin infusion. These matrices have attracted considerable interest since their introduction in 2013, and manufacturing trials have been performed for racing yachts and a wind turbine blade [7]. Results from tensile tests on the thermoplastic matrix indicated a modulus of around 3 GPa, which is similar to common epoxy resins [8]. Bhudolia et al. [9] found that carbon/Elium® laminates exhibited 72% higher Mode-I interlaminar fracture toughness than carbon/epoxy composites. However, there are still few publications reporting the mechanical properties of the infusible thermoplastics, or comparing them to well-established marine resin systems. Therefore, it is important to characterise the performance of the infusible thermoplastic resin as a potential candidate for selection in composite ship construction.

This needs to be done under a wide range of environmental conditions, as the durability of composites and their ability to exhibit unchanged performance and stability in a marine context and environment is a crucial factor in order to select the most appropriate combination of polymer matrix and reinforcement. Ideally, a composite would retain its mechanical and thermo-mechanical profile even when exposed to a marine environment for extended periods. During the service life of marine composites (typically 20–25 years [10]), water uptake is inevitable. This may cause plasticization, swelling, matrix hydrolysis or debonding of fibres from the matrix. As a result, the mechanical and thermal properties degrade accordingly, and the service life is shortened [11]. In composite materials with a brittle matrix, the damage mode can change from matrix-dominated before moisture absorption to fibre–matrix interfacial failure after saturation [12]. This leads to a significant change in the strength of composites. The Elium® matrix reportedly has a lower susceptibility to moisture uptake than epoxy matrices - Davies and Arhant [8] reported significantly lower equilibrium moisture content for glass/Elium® than for glass/epoxy composites (0.4% and 1.2%, respectively), and Chilali et al. [13] observed a similar result for flax/Elium® and flax/epoxy composites (6.6% and 7.3%, respectively). Composite materials in marine structures will also be exposed to corrosive liquids, such as engine oils and fuels, and it is important to evaluate the effect that exposure to a corrosive environment has on the mechanical properties of the material. Not much work has been done on the immersion of composite materials in vehicle oils, and there is no published study on the effect of immersion in oils of infusible thermoplastic composites at the time of writing. Amaro et al. [14] reported reductions of up to 11% in the flexural strength and 18% of the flexural modulus of glass/epoxy composite specimens exposed to engine oil for 45 days. The room temperature creep behaviour of glass/polyester composites exposed to water and lubricant oil for a period of six months was found to cause a 20% reduction in Young's modulus [15]. The specimens were also tested at 60 °C, where the large change in viscosity of the oil degraded the properties further than in the case of the specimens immersed in water, thereby demonstrating the need for an understanding of the effect of organic liquids (e.g. oils, diesel) on the properties of composite materials.

The performance of Elium® as a potential matrix for marine structural applications is not yet comprehensively documented. The development of infusible thermoplastics has created an opportunity to use materials that have a greater potential for recyclability without having to change the resin infusion equipment currently in place for manufacturing marine composite structures. Therefore, it is essential to characterise the mechanical properties of this resin system as a composite matrix, and determine if they are comparable to those of the well-established marine resin systems. While there is certainly more development required in terms of recovering the full value of long-fibre composite materials (i.e. separation of undamaged fibres and reusable matrix component) from end-of-life composite structures, increasing the potential for recovery and reusability of these materials is highly beneficial. Recyclability and recovery techniques are currently a popular and important research topic [2,16–20], but are outside the scope of this work. There is however a clear link between our work to characterise this commercially available infusible thermoplastic, and the current need to design composite structures with end-of-life disposal in mind.

The aim of this study is to assess the performance of an infusible thermoplastic matrix system compared to matrix materials most commonly used in marine structures under various immersion conditions. This work represents a part of a selection procedure to identify the most suitable materials for the construction of marine vessels over 50 m in length. Commercially available infusible thermoplastic, vinyl ester, polyester and epoxy resin systems were used to manufacture GFRP laminates using VaRTM. Mechanical properties of test coupons extracted from the laminates were assessed in relation to apparent interlaminar shear strength and dynamic mechanical properties. Properties of specimens under dry conditions and after an immersion period in deionised water and an organic liquid (diesel) were assessed to determine the effect of immersion on the performance of the materials.

2. Materials and methods

2.1. Materials

A range of state-of-the-art thermosetting resins and an infusible thermoplastic were studied as part of this work:

- 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-G-2 from Aliancys
- TP: Thermoplastic – Elium® 150 from Arkema

The properties and curing details of all matrix systems according to the manufacturer's datasheet are summarized in Table 1. The reinforcement fabrics used in this study were SAERTEX U-E−996g/m^2 unidirectional (UD) non-crimp glass fabric and SAERTEX U-E−940 g/m^2-LEO UD non-crimp glass fabric. The latter was used only with the LEO VE resin, as it is part of the LEO® composite system, comprising a bespoke and optimised sizing for the LEO VE resin. Both of the reinforcement fabrics used in this study have 90% of the glass fibres aligned with the 0° direction, the remaining glass fibres are oriented in the 90° direction to provide support to the dry reinforcement.

2.2. Laminate manufacture

All laminates were manufactured by placing the dry reinforcement fabric (with a $[0^\circ]_{2S}$ stacking sequence), 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. This approach commonly referred to as VaRTM has also been designated RIFT II in the literature [21] and is normally used for the manufacture of marine vessel components. All resin systems were infused without prior degassing at ambient temperature (approximately 20 °C). A vacuum pump was used

Table 1
Cured resin properties according to manufacturer datasheets

Description	EP	VE	PE	TP
Name (A)	Prime 27	Leo-*M*-8500	Synolite 8488-G-2	Elium 150
Curing Agent (B)	Prime 20 Slow Hardener	Butanox M-50	Butanox M-50	Perkadox CH-50X
Mass Ratio (A:B)	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 40min @25 °C	1hr 50min @20 °C	1hr 30min @23 °C	25min @25 °C
Curing time at ambient	24 h	24 h	24 h	24 h
Post-cure temperature	60 °C	80 °C	40 °C	Not Required
Post-cure time	7 h	6 h	16 h	Not Required
Heat deflection temperature	60–62 °C	105 °C	64 °C	109 °C
Tensile strength	74.3 MPa	95 MPa	70 MPa	76 MPa
Tensile modulus	3.5 GPa	3.6 GPa	3.8 GPa	3.3 GPa
Elongation at break	4.5%	6.1%	2.3%	6%

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 ratios of curing agent, curing and post-curing conditions for each system are shown in Table 1. The infusion time was measured from the opening of the resin inlet to the closure of the outlet (outlet was closed on observing bubble-free resin in the outlet tube). Infusion times to impregnate a preform of the size shown in Fig. 1 were approximately 20 min for all matrix systems. Test coupons were extracted using a water-cooled diamond-coated rotating disc cutter.

2.3. Environmental conditioning

All samples were dried for 4 h at 45 °C prior to testing. Wet condition samples were then immersed in deionised water at 35 °C for 28 days, in line with Lloyds Register Book K, Procedure 14-1, Rev 1 Dec 2013. Organic-wet condition samples were dried and then soaked in diesel fuel (standard grade road diesel) for seven days. For both wet and organic-wet conditions, specimens were weighed after drying to obtain the "dry mass" and after soaking to obtain the "soaked mass".

2.4. Experimental procedures

2.4.1. Physical properties

Fibre volume fraction (FVF) 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.

2.4.2. Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) was conducted using a TA Instruments Q800 Dynamic Mechanical Thermal Analyser with a three-point bend fixture in order to assess the viscoelastic properties of the composite specimens under dry, wet and organic-wet conditions. The specimens were heated from ambient temperature to 180 °C for dry and wet specimens and 150 °C for organic-wet specimens at a rate of 5 °C/min, with a displacement amplitude of 10 μm and at a frequency of 1 Hz. Storage modulus (E′), loss modulus (E″) and tan delta were recorded during the test. The T_g is taken as the tan delta peak temperature. One sample was tested for each condition.

2.4.3. Short Beam Shear

Short-span three-point bend Short Beam Shear (SBS) tests were conducted under quasi-static loading conditions in accordance with ISO 14130 to determine the apparent interlaminar shear strength (ILSS). Tests were performed using a Tinius Olsen Benchtop Tester (Model 25 ST) with a 10 kN load-cell (FL04224). Nominal specimen dimensions were 30 mm x 15 mm x 3 mm. A nominal span length of 15 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.

Cross-sections of tested SBS specimens were examined using a Hitachi SU-70 SEM at a voltage of 10 kV and a working distance of 10 mm, to determine if there was any change in the interlaminar failure mode due to the presence of water or the organic liquid. Specimens were mounted in a two-part epoxy (Epoxicure Resin and Epoxicure Hardener in a ratio of 5:1) with a conductive powder filler. Polished cross-sections

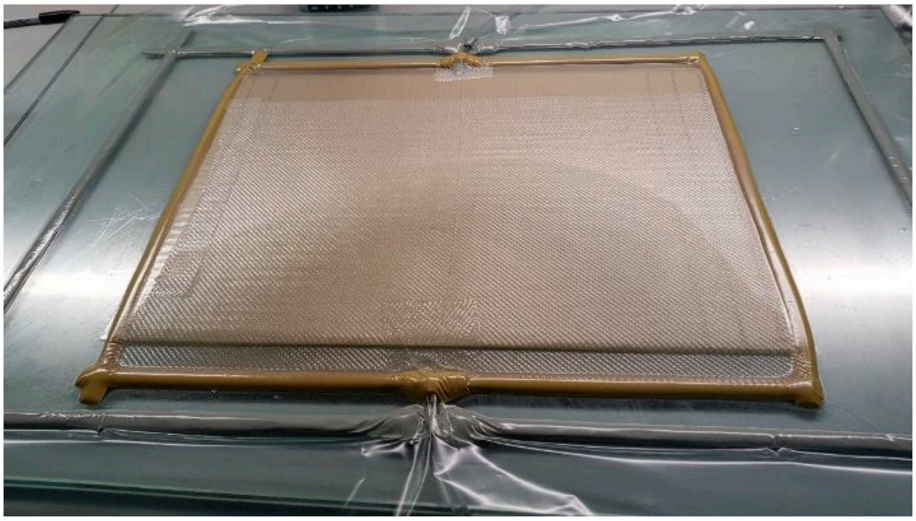


Fig. 1. Liquid Resin Infusion of glass fabric (500 mm wide x 350 mm long).

of SBS specimens were scanned and images from different locations along the plies were captured at different magnifications, in order to identify and assess the failure mechanism.

3. Results and discussion

3.1. Environmental conditioning and physical properties

The results of the water and diesel fuel uptake during immersion are summarised in Table 2. Two types of specimen (SBS and DMTA) were weighed before and after immersion to determine the amount of liquid uptake, which is expressed as a percentage of the dry specimen mass. The diffusion rate of the liquid into the specimen was not studied as part of this work.

The materials have similar cured ply thickness and similar FVF in the range of 52–55%. As the FVF for all specimens is similar, the quantity of water absorbed in the specimens can be compared directly – specimens with higher FVF tend to have lower potential for water uptake as the fibres hamper the water diffusion channel, which slows the diffusion rate of water molecules in composites [11]. The water uptake for the EP specimens is 24% higher than that of the TP specimens, which is similar to published results [8,13]. However, the diesel fuel uptake is within the same range for both materials. It can be seen that the VE and PE specimens had the lowest water uptake of all materials studied. The VE's low moisture uptake could potentially be influenced by the custom sizing on the glass fibres in the VE (LEO system) fabric. Wang et al. reported that carbon/epoxy composite specimens that had a fibre sizing that was designed to be compatible with the matrix absorbed less moisture than those that did not. The interface between the fibre and the matrix is therefore easier to debond or crack under attack by water molecules, which ultimately increases the moisture volume [22]. 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. The uptake of diesel fuel is low – partly due to the short immersion time – with the EP and TP having comparable results; the VE and PE had higher uptake than the EP and TP.

3.2. Dynamic Mechanical Thermal Analysis

During this study, DMTA was primarily used as a tool to ensure that laminates had reached a fully cured state before proceeding to mechanical testing. None of the laminates showed signs of ongoing post-cure, and hence all mechanical testing was carried out thereafter. The results of the DMTA tests for all materials under dry, wet and organic-wet conditions are shown in Table 3, and E' curves for all specimens in the dry, wet and organic wet state are shown in Fig. 2. The glass transition temperature (T_g) was taken as the temperature corresponding to the peak in the tan delta curve.

The storage modulus is a measure of elasticity: the onset temperature is the temperature at which the storage modulus drops dramatically indicating a loss in rigidity and hence defines the service temperature ceiling of the material. Tan delta is known as the damping parameter and is an indication of the viscoelastic damping behaviour of the composite material. The peak of the tan delta curve occurs due to the relaxation of the polymer chains, and, as stated previously, the corresponding temperature is considered as the T_g [23].

In the dry condition, the TP specimens had the highest onset temperature, which significantly exceeded all other systems, and the EP specimens had the lowest. Immersion in water was observed to have reduced the onset temperatures of all materials. The VE and PE materials had similar water uptake (0.26%) yet significantly different reductions in onset temperatures (−18.5% and −3.3% respectively) and glass transition temperatures (−9.7% and −3.8% respectively). We postulate that the fibre sizing has been optimized for the VE fibre-sizing-matrix system for ambient temperatures. However, the sizing may not be optimized for the VE material at elevated temperatures in the wet condition where a significant reduction in the onset temperature (−18.5%) and T_g (−9.7%) is evident. While further investigation was outside the scope of this study, we can also postulate that significant damage (such as interfacial fibre-matrix debonding, matrix cracking, plasticisation or a combination) is induced in the VE material under hot-wet conditions which reduces the storage modulus/dynamic stiffness of the VE laminate. The damage induced in the PE under hot-wet conditions has a less pronounced effect on the onset temperature and T_g. Dicyclopentadiene-based polyesters would be expected to be highly hydrophobic due to the presence of the non-polar dicyclopentadiene units. This very hydrophobic matrix may be significant in counteracting adverse effects of water ingress under hot-wet conditions for the PE laminate.

The TP system had only a moderate drop in onset temperature (−11%) compared to the VE, which is promising considering the water uptake was higher (0.45%). EP, VE and TP systems experience a reduction in T_g between 9% and 12%, while the T_g of the PE system was reduced by 4%. The reduction in the T_g indicates that less energy is required to cause large scale motion of the polymer chains during the glass-rubber transition. This could be caused by the molecules of the immersion liquid occupying the free volume between the polymer chains, plasticising the matrix and increasing molecular movement. Alternatively, the absorbed water may induce cracking and fibre-matrix debonding due to the mismatch in the moisture expansion coefficients between the fibre and the matrix [22].

Organic-wet specimens exhibited no significant change in the onset temperature except in the case of PE which displayed the largest reduction (−11%) in onset temperature under hot/organic-wet conditions, even though the uptake of the organic wet liquid for PE (0.08%) is marginally lower than VE (0.14%). Similar to the wet case, we postulate that damage (such as interfacial fibre-matrix debonding, matrix cracking, plasticisation or a combination) is induced under hot/organic-wet conditions compromising the storage modulus/dynamic stiffness of the laminate. As PE comprises a highly apolar, hydrocarbon-based matrix, it would be expected that it would show the highest affinity for diesel amongst all resin systems, with hot/organic-wet conditions causing more pronounced damage compared to all other laminates.

3.3. Interlaminar shear strength

Fig. 3 presents a summary of the apparent ILSS values for all specimens under dry, wet and organic-wet conditions. SEM images of the tested SBS specimens under dry, wet and organic-wet conditions for EP, VE, PE and TP specimens, as well as a schematic of the specimen indicating the approximate location of cracks, are shown in Figs. 4–7, respectively.

There is a clear separation in terms of the dry performance – the EP and TP exhibit comparable high values while the VE and PE have comparable, lower values. The SBS test is designed to yield information regarding the interlaminar shear strength, which is directly influenced by the mechanical strength of the fibre/matrix interface.

Table 2
Summary of the cured ply thickness, fibre volume fraction (FVF), average water uptake and average diesel fuel uptake of each material tested.

Material	Cured Ply Thickness	FVF	Average Water Uptake (28 days, 35°C)	Average Diesel Fuel Uptake (7 days, 23°C)
VE	0.71 mm	52%	0.26% ± 0.07%	0.14% ± 0.03%
PE	0.73 mm	54%	0.26% ± 0.02%	0.08% ± 0.07%
EP	0.74 mm	53%	0.56% ± 0.03%	0.03% ± 0.03%
TP	0.72 mm	55%	0.45% ± 0.04%	0.02% ± 0.02%

Table 3
Onset and Glass Transition Temperatures for EP, VE, PE and TP composite laminates.

Material	Onset Temperature (°C)			Tg (°C)		
	Dry	Wet*	Organic Wet*	Dry	Wet*	Organic Wet*
EP	76.2	60.1 (-21.1%)	76.7 (+0.6%)	85.1	75.7 (-11.3%)	85.0 (-0.1%)
VE	82.7	67.4 (-18.5%)	78.8 (-4.7%)	100.2	90.5 (-9.7%)	98.4 (-1.8%)
PE	85.8	83.0 (-3.3%)	76.4 (-11.0%)	104.3	100.3 (-3.8%)	101.3 (-2.9%)
TP	96.3	85.7 (-11.0%)	94.9 (-1.5%)	115.2	102.8 (-10.8%)	112.5 (-2.3%)

* 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.

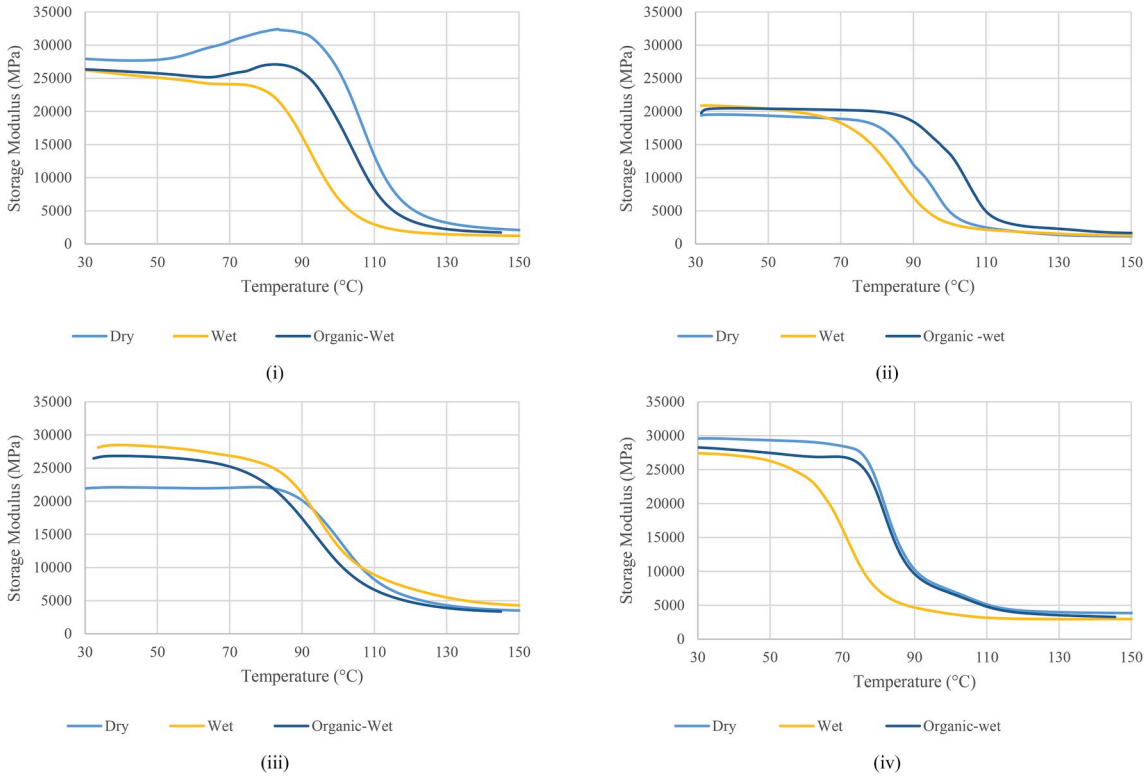
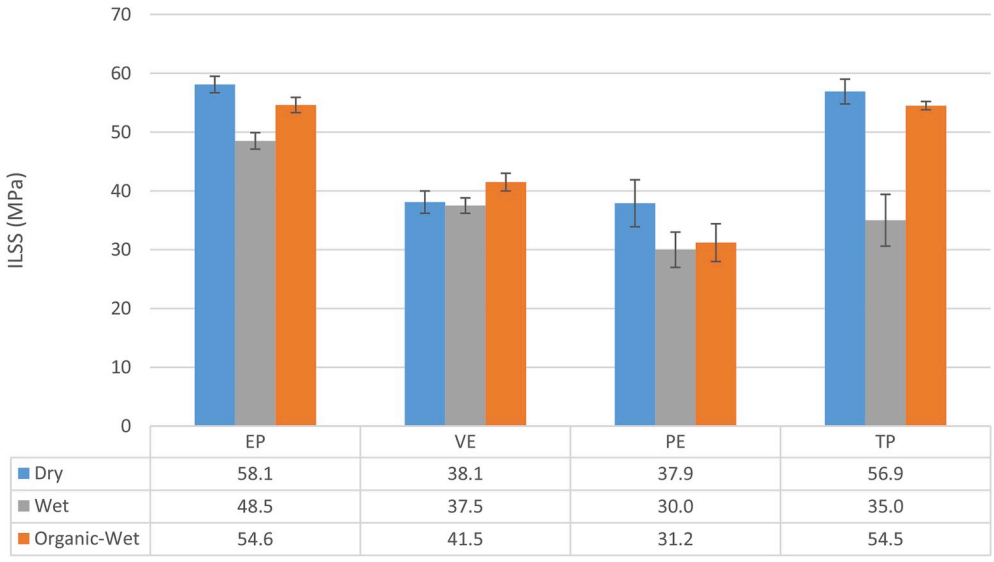


Fig. 2. Storage Modulus for the dry, wet and organic wet specimens over a temperature increase for (i) Thermoplastic, (ii) Vinyl Ester, (iii) Polyester and (iv) Epoxy composites.

The largest reduction in ILSS due to immersion in water is in the TP system (37%) and is a clear indication of the negative effect of the water on the fibre-matrix interface. This is evident from the SEM images (Fig. 7) showing the fracture in the dry, wet and organic-wet TP SBS specimens; the dry specimen fails due to matrix-dominant crack growth, while the failure occurs along the weakened fibre-matrix interface in both wet and organic-wet immersed specimens. The TP specimens are the only specimens to exhibit a change in failure location from matrix to fibre-matrix interface. This would suggest that the performance could potentially be improved if the infusible thermoplastic resin is used in conjunction with a fibre carrying a sizing that is specifically tailored to be chemically compatible with an acrylic-based thermoplastic resin. Boufaida et al. [20] found that the application of a coupling agent specifically developed for promoting the bond between glass fibres and acrylic resins improved the composite mechanical properties.

The PE and EP systems also exhibited significant reductions in water (21% and 16%, respectively). To this end, the benefit of the tailored sizing of the LEO fabric is noticeable – the VE composite specimens experience the smallest change (2%) in ILSS regardless of immersion in water. The failure mode for VE (Fig. 5) and PE (Fig. 6) specimens was similar; interfacial cracks were present in the 90° fibre bundles. However, the tailored fibre sizing used in the VE laminate enabled much higher shear strength retention in the wet (−2%) compared to the PE material (−21%).

Dry EP specimens (Fig. 4) exhibited micro-buckling/kinking in the upper ply of the specimen, which is indicative of strong interfacial



	EP	VE	PE	TP
Dry	58.1	38.1	37.9	56.9
Wet	48.5	37.5	30.0	35.0
Organic-Wet	54.6	41.5	31.2	54.5

Fig. 3. Summary of the results for the apparent ILSS of each material system under dry, wet and organic-wet conditions.

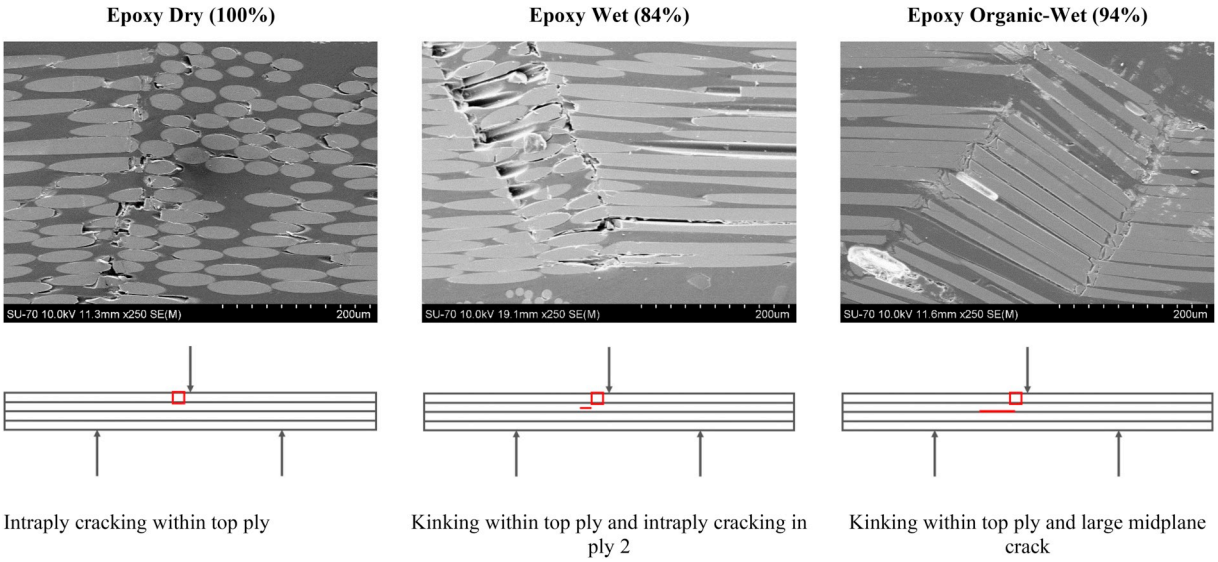


Fig. 4. SEM images of tested epoxy SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

bonding. Wet and organic-wet EP failed specimens also exhibited buckling and, due to conditioning in both mediums, mid-plane cracks. This indicates that the interface has weakened due to the presence of water or organic liquid. While buckling is still occurring at the compressive side of the specimen, the interface has been weakened sufficiently for the shear stress at the mid-plane to cause cracking in the wet and organic-wet EP specimens.

The SEM images in Figs. 4–7 show that the organic-wet specimens invariably showed a similar failure mode to the wet specimens. However, organic-wet specimens experienced failure in multiple locations with shorter cracks throughout the specimen, whereas dry and wet specimens typically failed in one location due to a relatively long crack. The location of the cracks in the organic-wet specimens also indicates a weakening of the fibre-matrix interface. In specimens with high interlaminar strength (e.g. dry EP in Fig. 4) the damage also occurred at the compressive side of the specimen; however, as previously mentioned, immersion in organic liquid weakens the fibre-matrix interface and the critical damage appears at the mid-plane where the interfacial shear is highest. In general, the effect of short term immersion in an organic liquid is low (approximately 5% change from the "dry" value) in all systems except for the PE system (−18%). While the fibre sizing is optimized for the VE system under ambient conditions, this is not the case for the PE laminates and leads to poor retention of shear strength. While the PE resin is approved by some authorities for marine applications, the importance of considering the fibre-sizing-matrix system rather than just the matrix alone is apparent.

4. Conclusion

The aim of this study was to evaluate the performance of a range of thermosetting resins and an infusible thermoplastic resin as part of a comprehensive down-selection to identify suitable commercially available resin systems for the manufacture of marine vessels greater than 50 m in length. It was of interest to investigate if the infusible

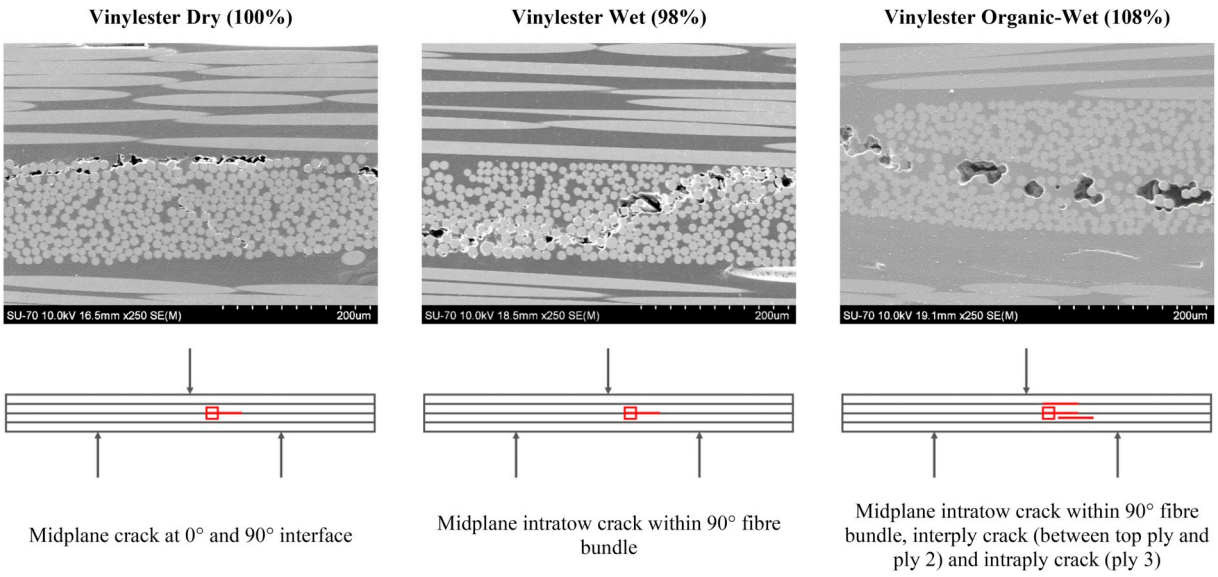


Fig. 5. SEM images of tested vinylester SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

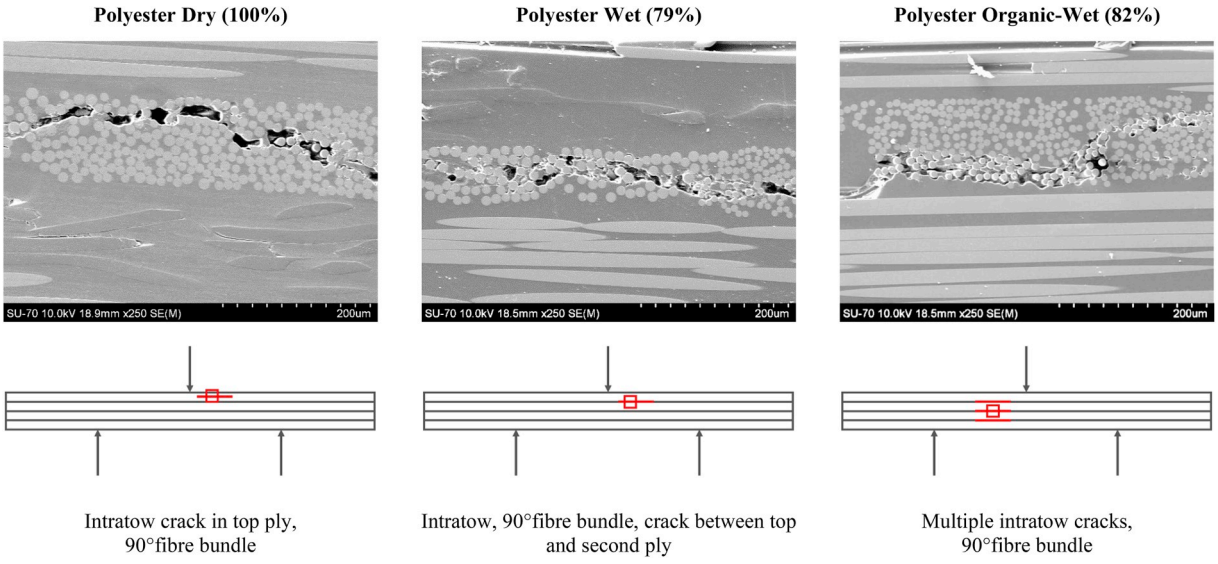


Fig. 6. SEM images of tested polyester SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

thermoplastic exhibits mechanical properties that are comparable to the matrix materials most commonly used in marine structures (i.e. epoxy, vinyl ester and polyester) as it has the potential to reduce the end-of-life environmental impact of the composite material. Apparent ILSS and DMTA properties were assessed under dry conditions and after a period of immersion in deionised water and an organic liquid. The key findings of this study are:

- The materials have similar cured ply thickness and similar FVF in the range of 52–55%. EP had a water uptake 24% higher than that of the TP specimens, which was similar to published results. VE and PE had the lowest water uptake of all materials – their values were similar and almost half of EP water uptake value.VE had the highest uptake of organic liquid and TP the lowest uptake.
- In terms of performance in the dry condition, the TP showed comparable properties to, and even exceeded the performance of the EP. The TP had the highest onset temperature and T_g indicating that it can maintain stiffness to higher temperatures than the other materials, while the EP had the lowest of both temperatures. The EP and TP exhibit comparable high ILSS values while the VE and PE have comparable, lower values. SEM showed that the failure in the EP specimens occurred due to buckling on the compressive face of the SBS specimen, which occurs when the interfacial strength is high and the specimen fails due to buckling instead of at the mid-plane where interfacial shear is highest. TP specimens failed at the mid-plane with the failure being matrix-dominated and the PE and VE specimens failed in the 90° fibre tows.
- In terms of performance in the wet condition, VE specimens showed no significant changes in terms of ILSS. The failure mode in the SBS

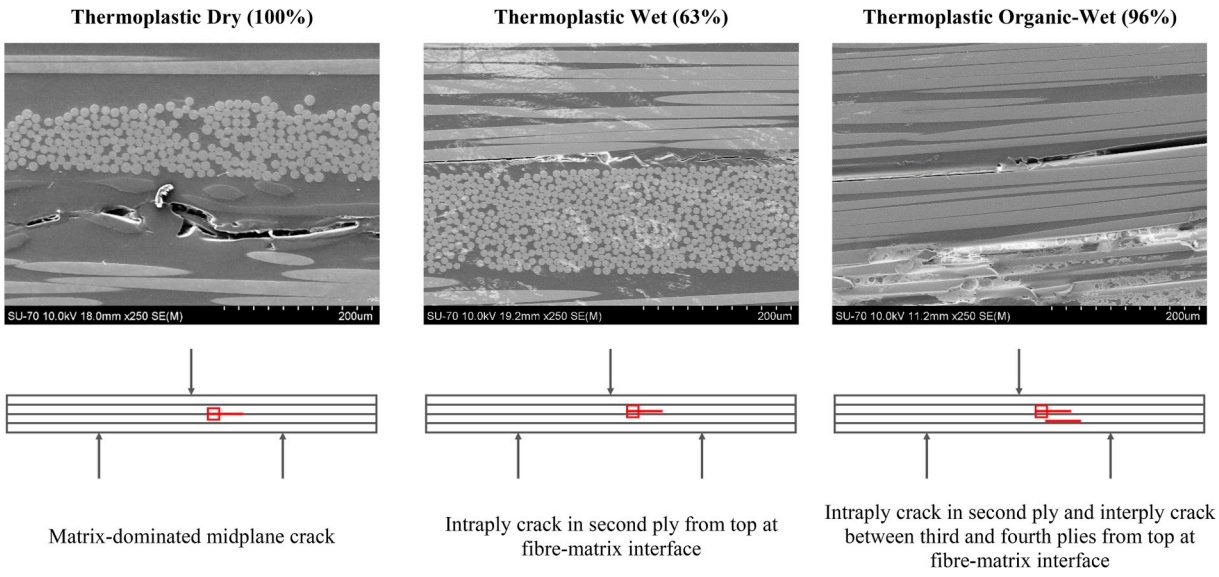


Fig. 7. SEM images of tested thermoplastic SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

specimens was observed in the SEM to remain the same as that observed for the dry specimens. This was attributed to the VE specimens having a strong fibre-matrix interface as the resin and fabric are part of a commercially available composite system and are designed to be compatible with one another. The PE and EP systems exhibited significant reductions in ILSS (21% and 16%, respectively); however, the largest reduction was observed in the TP specimens (37%). This was attributed to a poor fibre-matrix interface as the failure was observed to transition from matrix-dominated in the dry state to interfacial in the wet state.

- In terms of performance in the organic-wet condition, there was no significant change in onset temperature or T_g due to immersion in organic liquid except in the case of the onset temperature for PE. This reduction was attributed to pronounced damage occurring due to the combination of high PE resin affinity for diesel and hot/organic-wet conditions, which in turn reduced the dynamic stiffness of the material. PE also exhibited a drop in ILSS under ambient conditions (−18%). Damage was clearly in the form of multiple short cracks for the VE, PE and TP materials. In contrast, dry and wet SBS specimens consistently showed only one long crack in the tested specimens. In addition, organic wet EP specimens exhibited failure at the midplane (due to high interfacial shear) as opposed to primarily localised buckling at the loading point as observed in the dry and wet specimens. This suggests a reduction in interfacial strength due to the presence of the organic liquid meaning that failure occurred at the interface before buckling could occur at the loading point.

Overall, the infusible TP exhibited good material properties and compared well with the EP in the dry condition. However, poor interfacial strength observed particularly in the wet specimens meant that there were large reductions in ILSS. Despite the large reductions after the immersion period, the performance of the wet specimens was still comparable with the VE and PE in the SBS tests. The benefits of using a specifically tailored interface was exhibited in the performance of the VE across the three test conditions, hence the performance of the TP could potentially be improved if coupled with a fibre that is sized to be compatible with acrylic-based resin systems. It has been demonstrated that the infusible TP system could be a candidate for use in marine structures – with the added benefit of reuse at end-of-life – provided the fibre-matrix interface can be tailored to improve performance over a range of environmental conditions. 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesb.2019.107271.

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