Effect of Environmental Conditioning on the Properties of Thermosetting- and Thermoplastic-Matrix Composite Materials by Resin Infusion for Marine Applications

N.H. Nash[a], A. Portela[a], C. Bachour[a], I. Manolakis[a], A.J. Comer[a,b*]

[a]Irish Composites Centre (IComp), Bernal Institute, University of Limerick, Limerick, Ireland
[b]School of Engineering, University of Limerick, Limerick, Ireland

*Corresponding Author: Anthony.comer@ul.ie

Keywords: Glass-fibre reinforced polymer; Thermosetting Resin; Thermoplastic Infusible Resin; Marine Composites; Environmental Conditioning

Abstract

Glass-fibre reinforced polymer (GFRP) laminates were manufactured using Vacuum assisted Resin Transfer Moulding (VaRTM) with a range of thermosetting resins and a novel 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 they are extensively used in the marine industry for the manufacture of lightweight hull structures (currently only in vessels up to 50 m in length with some exceptions), secondary structures and components. 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.

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 around 3 GPa, 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 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 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 creep behaviour of glass/polyester composites exposed to water and lubricant oil for a period of six months was found by Souza *et al.* [15] to be affected due to a 20% reduction in Young's Modulus when tested at room temperature. 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 (i.e. oils, diesel, etc.) 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 novel 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 with 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 large-length ship construction. Commercially available vinyl ester, polyester and epoxy resin systems and a novel infusible thermoplastic were used to manufacture GFRP laminates using Vacuum assisted Resin Transfer Moulding (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 a novel infusible thermoplastic were studied as part of this work:

- EP: Epoxy - PRIME^{TM} 27 from Gurit
- VE: Vinylester - LEO Injection Resin 8500 from BÜFA (this resin is part of the Saertex LEO® fire retardant composite system)
- PE: Polyester - Synolite 8488-G 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, where the benefits of the thermoplastic system over the thermosetting systems in terms of faster gel times, high temperature performance and the absence of post-cure requirements are evident. 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. 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.

Table 1: Cured resin properties according to manufacturer datasheets

Description	EP	VE	PE	TP
Name (A)	Prime 27	Leo-M-8500	Synolite 8488-G	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 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
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%

2.2 Laminate Manufacture

All laminates were manufactured on a glass tool using a $[0°]_{2S}$ stacking sequence. All resin systems were infused at ambient temperature (approximately 20°C). 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 Figure 1 were approximately 20 minutes for all matrix systems. Test coupons were extracted using a water-cooled diamond-coated rotating disc cutter.

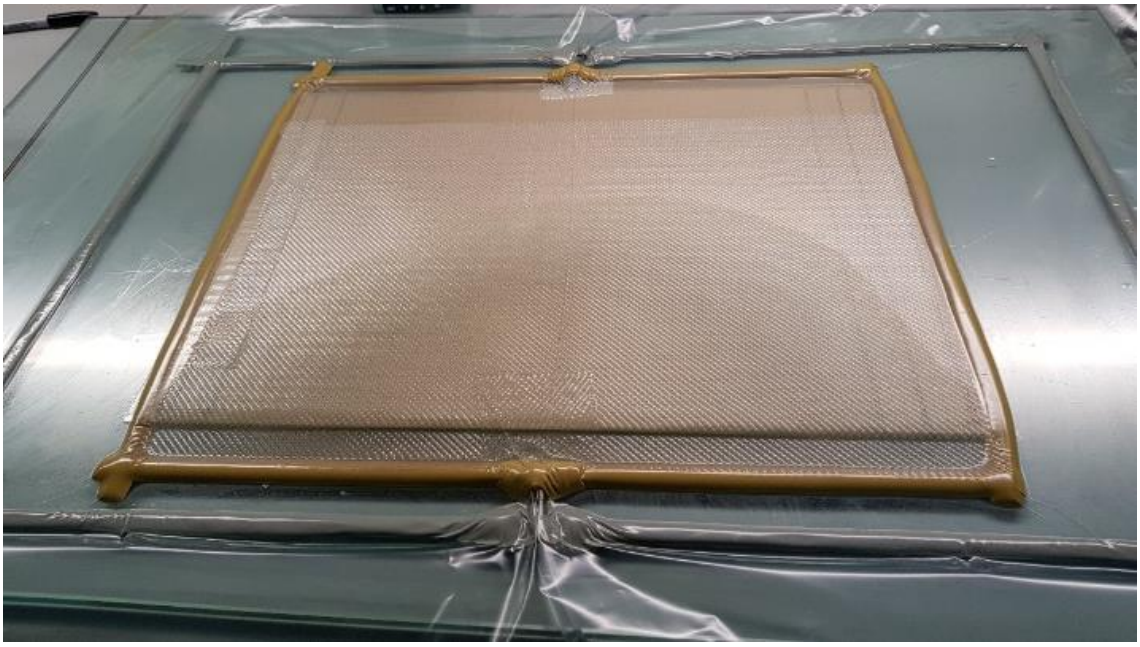


Figure 1: Liquid Resin Infusion of glass fabric (500 mm wide x 350 mm long)

2.3 Environmental Conditioning

All samples were dried for four hours at 45 °C prior to testing. Wet condition samples were then immersed in distilled 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 then soaked in diesel fuel 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.

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). 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. Cross-sections of tested SBS specimens were examined using a Hitachi SU-70 at a voltage of 10 kV 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.

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.

Table 2: Summary of the cured ply thickness, fibre volume fraction, 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%

The materials have similar cured ply thickness and similar FVF in the range of 52-55%, which is typical for the VaRTM manufacturing method. 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. 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. While the moisture content at this point for the PE is lower than expected, 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 [21]. 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. 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. 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 EP and VE systems were observed to have a large drop (~20%) in the temperature to which stiffness could be maintained. The PE system only had small changes in the onset temperature and storage modulus due to the presence of water in the specimens. This could be attributed to a combination of having a comparatively low moisture uptake (Table 2) a. The TP system, however, had a moderate drop in onset temperature (11%). These reductions in the

temperature associated with the retention of the stiffness component of the composite materials are an indication of matrix plasticisation. Organic-wet specimens exhibited no significant change in the onset temperature, except in the case of the PE (-11%).

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 [22]. 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 due to the mismatch in the moisture expansion coefficients between the fibre and the matrix [21].

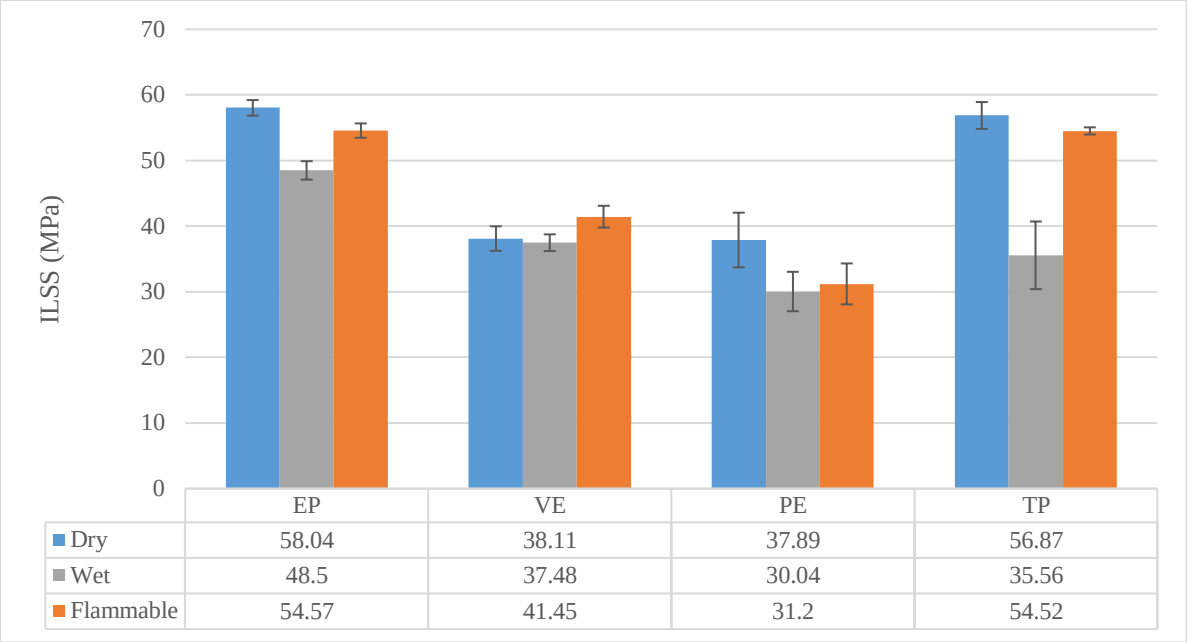
Table 3: Onset and Glass Transition Temperatures for EP, VE, PE and TP composite laminates.

Material	Onset Temperature (°C)			Tg (°C)		
	Dry	**Wet***	**Flam***	**Dry**	**Wet***	**Flam***
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.

3.3 Interlaminar Shear Strength

Figure 4 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 Figure 5, 6, 7 and 8, respectively.



	EP	VE	PE	TP
Dry	58.04	38.11	37.89	56.87
Wet	48.5	37.48	30.04	35.56
Flammable	54.57	41.45	31.2	54.52

Figure 2: Summary of the results for the apparent ILSS of each material system under dry, wet and organic-wet conditions

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 give information regarding the interlaminar shear strength, which is directly influenced by the mechanical strength of the fibre/matrix interface. 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 (Figure 8) 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 PE and EP systems also experience significant reductions in ILSS (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 despite the immersion period. 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 failure mode for VE (Figure 6) and PE (Figure 7) specimens was similar; cracks were present in the 90° fibre bundles. Large changes in direction of the fibres within a laminate create stress concentrations due to localised variations in elastic properties. Dry EP specimens (Figure 5) consistently failed due to buckling in the upper ply of the specimen. This indicates a strong interfacial bond as the specimens fail due to

buckling/kinking of the plies on the compression-side of the specimen. 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 force at the mid-plane to cause cracking in the wet and organic-wet EP specimens.

The effect of the organic liquid on the ILSS is low (approximately 5% change from the "dry" value) in all systems except for the PE system. This could again be potentially linked to the negative change in mass reported in Section 3.1, which suggested that some degradation might be occurring during immersion. The SEM images in Figures 5-8 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 Figure 5) the critical damage will occur at the compressive side of the specimen; however, as previously mentioned, immersion in organic liquid weakens the interface and the critical damage starts to also appear at the mid-plane where the interfacial shear is highest.

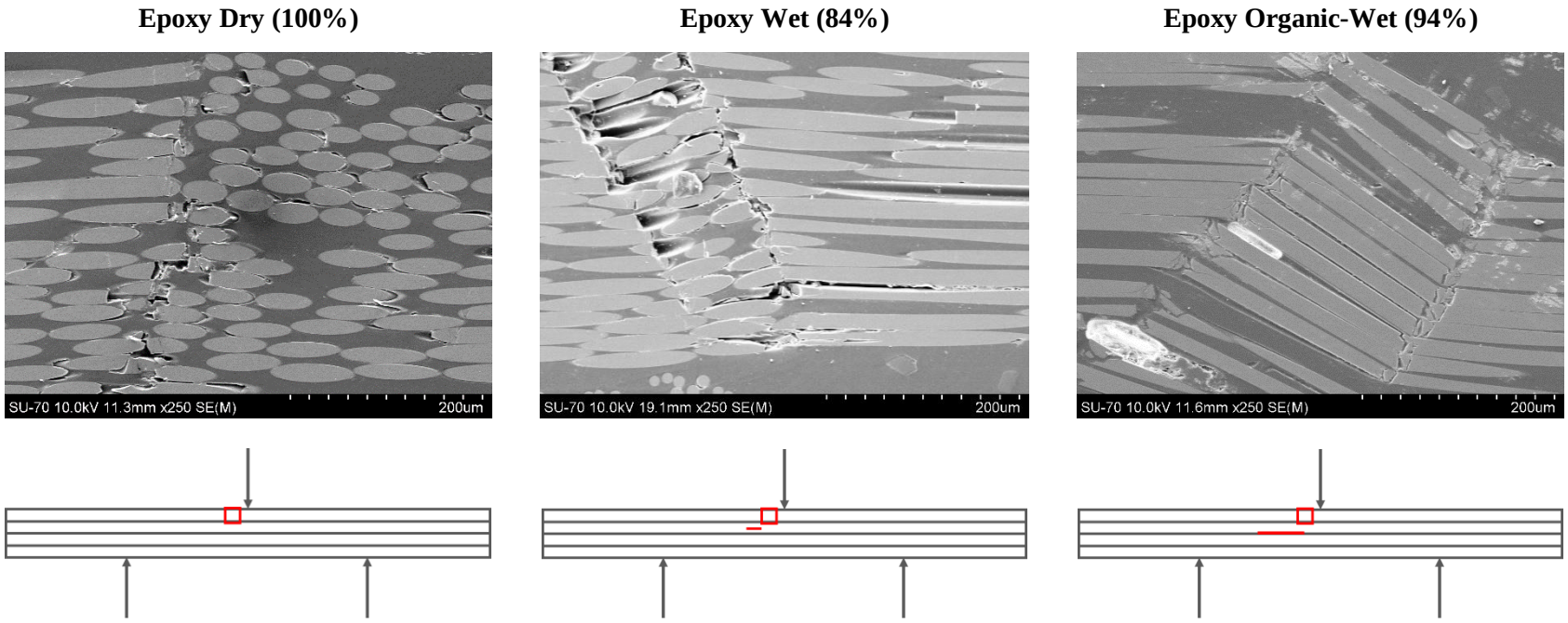
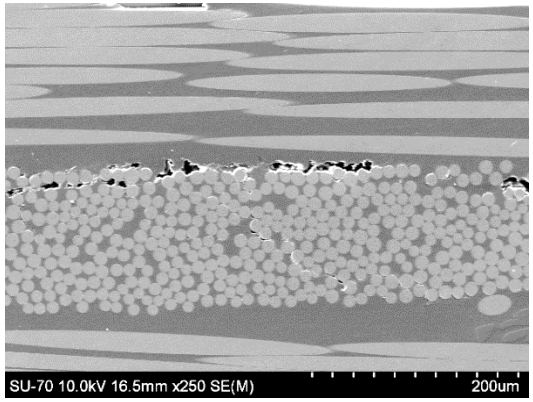
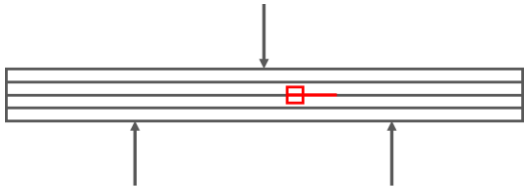


Figure 3: SEM images of tested epoxy SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed.

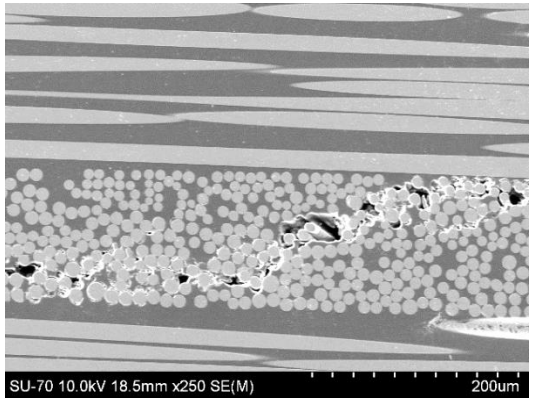
Vinylester Dry (100%)

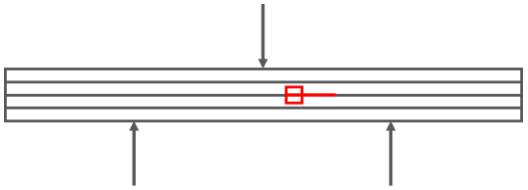




Midplane crack at 0° and 90° interface

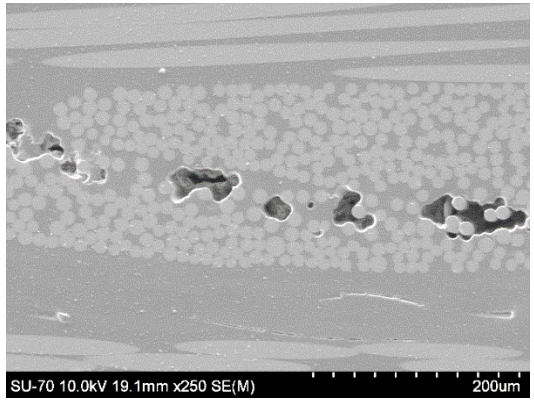
Vinylester Wet (98%)

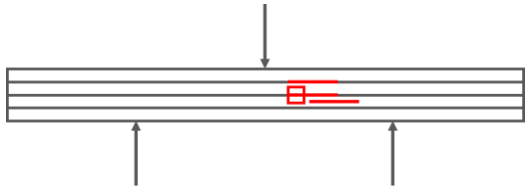




Midplane intratow crack at 0° and 90° interface

Vinylester Organic-Wet (108%)

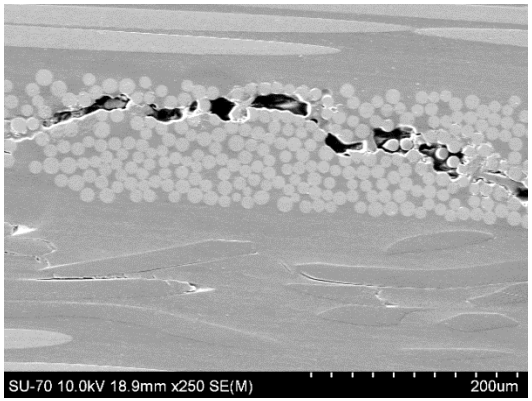


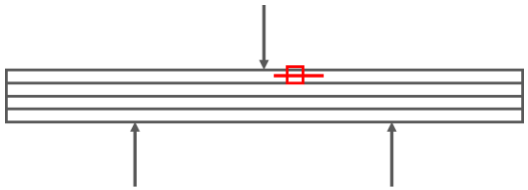


Midplane intratow crack at 0° and 90° interface, interply (ply 1 – top ply – and 2) and intraply cracks (ply 3)

Figure 4: 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

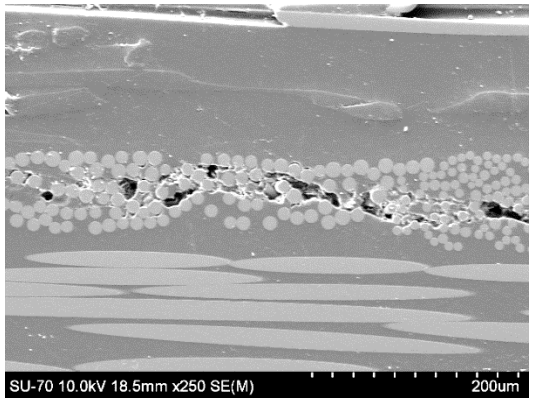
Polyester Dry (100%)

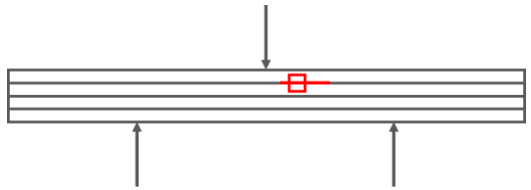




Intratow crack in top ply, 90°fibre bundle

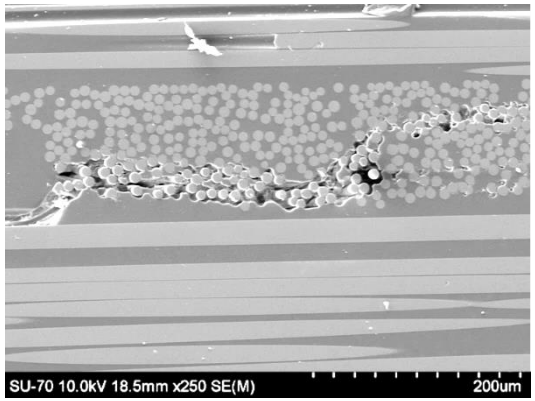
Polyester Wet (79%)

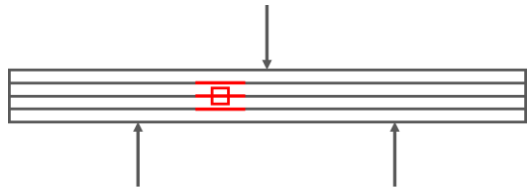




Intratow, 90°fibre bundle, crack between top and second ply

Polyester Organic-Wet (82%)





Multiple intratow cracks, 90°fibre bundle

Figure 5: 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

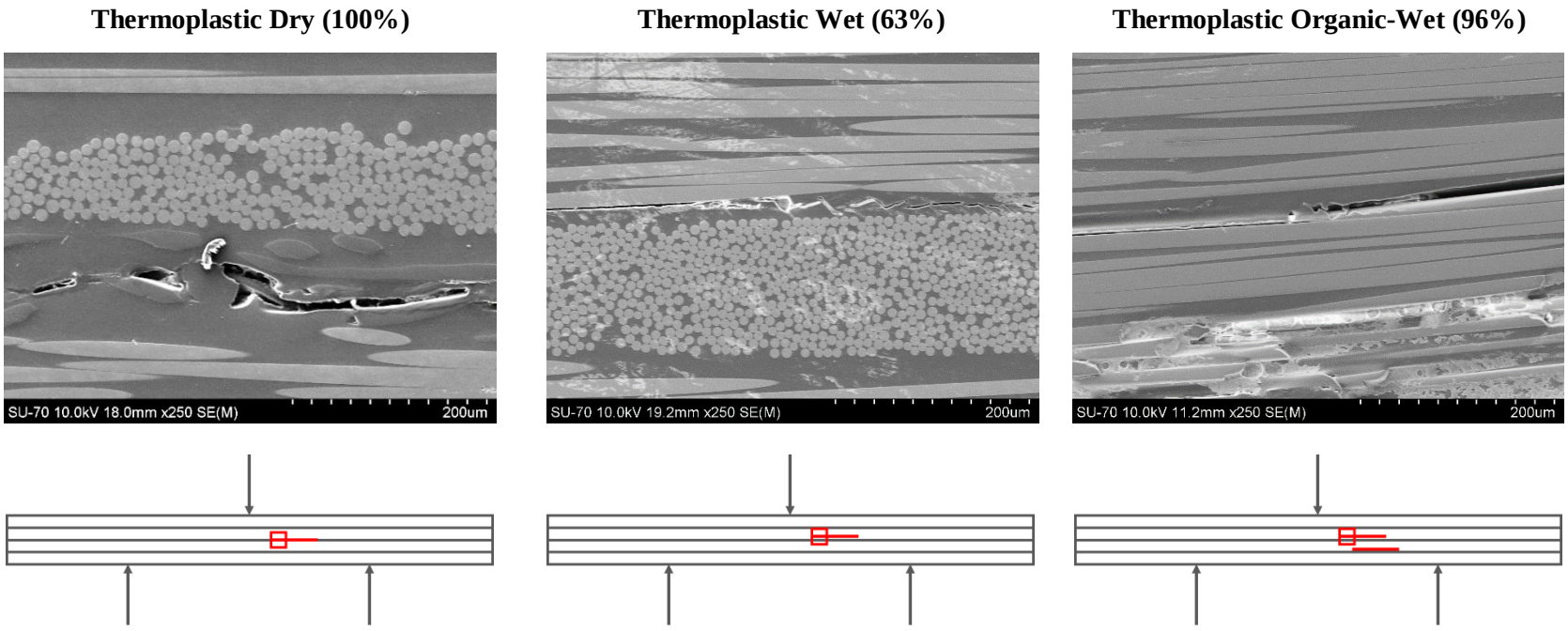


Figure 6: SEM images of tested thermoplastic SBS specimens under dry, wet and organic wet conditions. The damage observed in each specimen is illustrated schematically and described briefly. The area captured in the SEM image is highlighted in the red box on the SBS schematic. The percentage indicates the percentage of the dry ILSS value at which the sample failed

4 Conclusion

The aim of this study was to evaluate the performance of a range of thermosetting resins and a novel 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 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 distilled 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%, which is typical for the VaRTM manufacturing method. EP had an 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. Organic liquid uptake was similar for all materials.
- 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 at the intersection of 0° and 90° fibres due to a stress concentration caused by the sudden change in directional material properties.
- In terms of performance in the wet condition, VE specimens showed no significant changes in onset temperature, T_g, or ILSS. The failure mode in the SBS specimens was observed in 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 EP and PE specimens had large (~20%) drops and the TP had a moderate (11%) reduction in onset temperature due to the presence of moisture which could indicate matrix plasticisation. The PE and EP systems also experience 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.

- There was no significant change in onset temperature or T_g due to immersion in organic liquid except in the case of PE, which was the only material to record a reduction in mass after immersion. There was no significant change in the ILSS (except in the case of PE, which could potentially have undergone degradation during the immersion period) however, large-scale damage was observed in SEM images of the SBS specimens in the form of multiple short cracks. In contrast to this, dry and wet SBS specimens consistently had only one long crack in the tested specimens. In addition, organic wet EP specimens exhibited failure at the mid-plane (due to high interfacial shear) as opposed to primarily compressive failure in the dry and wet specimens, suggesting a reduction in interfacial strength.

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 the promising TP acrylic matrix.

Acknowledgment

The authors would like to acknowledge that this work is funded under the Horizon 2020 programme through the FIBRESHIP project (Project ref: 723360).

References

[1] AVK/Carbon Composites, 2017. Composites Market Report 2017. [Online] Available at: http://www.eucia.eu/userfiles/files/20170919_avkccev__market_report_2017.pdf [Accessed 7 8 2018].

[2] Naqvi, S. et al., 2018. A critical review on recycling of end-of-life carbon fibre/glass fibre reinforced composites waste using pyrolysis towards a circular economy. Resources, Conservation and Recycling, Volume 136, pp. 118-129.

[3] Yang, Y. et al., 2012. Recycling of composite materials. Chemical Engineering and Processing: Process Intensification, Volume 51, pp. 53-68.

[4] Directive 2000/53/EC on end-of-life vehicles. Official Journal of the European Union, L 269/34, 21.10.2000

[5] Rybicka, J., Tiwari, A. & Leeke, G. A., 2016. Technology readiness level assessment of composites recycling technologies. Journal of Cleaner Production, 112(1), pp. 1001-1012.

[6] Otheguy, M. et al., 2009. Recycling of End-of-Life Thermoplastic Composite Boats. Plastics, Rubber and Composites, 38(9-10), pp. 406-411.

[7] Arkema, 2018. Elium® for infusion. [Online] Available at: https://www.arkema.com/en/products/product-finder/product-viewer/Elium-for-infusion/[Accessed 10 8 2018].

[8] Davies, P. & Arhant, M., 2018. Fatigue Behaviour of Acrylic Matrix Composites: Influence of Seawater. Applied Composite Materials, pp. 1-12.

[9] Bhudolia, S. K., Perrotey, P. & Joshi, S. C., 2018. Mode I fracture toughness and fractographic investigation of carbon fibre composites with liquid Methylmethacrylate thermoplastic matrix. Composites Part B: Engineering, Volume 134, pp. 246-253.

[10] Summerscales, J., Graham-Jones, J. & Pemberton, R., 2018. Marine Composites. 1st ed. UK: Woodhead Publishing.

[11] Xian, G., Li, H. & Su, X., 2012. Water Absorption and Hygrothermal Ageing of Ultraviolet Cured Glass-Fiber Reinforced Acrylate Composites. Polymer Composites, 33(7), pp. 1120-1128.

[12] Afshar, A., Liao, H.-T., Chiang, F.-p. & Korach, C. S., 2016. Time-dependent changes in mechanical properties of carbon fiber vinyl ester composites exposed to marine environments. Composite Structures, Volume 144, pp. 80-85.

[13] Chilali, A. et al., 2018. Effect of water ageing on the load-unload cyclic behaviour of flax fibre-reinforced thermoplastic and thermosetting composites. Composite Structures, Volume 183, pp. 309-319.

[14] Amaro, A., Reis, P., Neto, M. & Louro, C., 2014. Effect of different commercial oils on mechanical properties of composite materials. Composite Structures, Volume 118, pp. 1-8.

[15] Souza, L. d., Marques, A. & d'Almeida, J., 2017. Effects of aging on water and lubricating oil on the creep behavior of a GFRP matrix composite. Composite Structures, Volume 168, pp. 285-291.

[16] Verma, S., Balasubramaniam, B. & Gupta, R. K., 2018. Recycling, reclamation and re-manufacturing of carbon fibres. Current Opinion in Green and Sustainable Chemistry, Volume 13, pp. 86-90.

[17] Ayre, D., 2018. Technology advancing polymers and polymer composites towards sustainability: A review. Current Opinion in Green and Sustainable Chemistry, Volume 13, pp. 108-112.

[18] Khalil, Y., 2018. Comparative environmental and human health evaluations of thermolysis and solvolysis recycling technologies of carbon fiber reinforced polymer waste. Waste Management, Volume 76, pp. 767-778.

[19] Dong, P. A. V., Azzaro-Pantel, C. & Cadene, A.-L., 2018. Economic and environmental assessment of recovery and disposal pathways for CFRP waste management. Resources, Conservation and Recycling, Volume 133, pp. 63-75.

[20] Boufaida, Z., Farge, L., André, S. & Meshaka, Y., 2015. Influence of the fiber/matrix strength on the mechanical properties of a glass fiber/thermoplastic-matrix plain weave fabric composite. Composites Part A: Applied Science and Manufacturing, Volume 75, pp. 28-38.

[21] Wang, Z., Xian, G. & Zhao, X.-L., 2018. Effects of hydrothermal aging on carbon fibre/epoxy composites with different interfacial bonding strength. Construction and Building Materials, pp. 634-648.

[22] Nash, N., Ray, D., Young, T. & Stanley, W., 2015. The influence of hydrothermal conditioning on the Mode-I, thermal and flexural properties of Carbon/Benzoxazine composites with a thermoplastic toughening interlayer. Composites Part A: Applied Science and Manufacturing, Volume 76, pp. 135-144.