Bio-based epoxy resin systems as potential alternatives to petroleum-based epoxy matrices in marine fibre-reinforced polymer composites

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Introduction

Fibre-reinforced polymers (FRP) are extensively used in the marine industry for the manufacture of lightweight hull structures for vessels up to 50 m in length, and for secondary structures and components in larger vessels. The main benefits resulting in the application of FRP in shipbuilding include: significant weight reduction resulting in substantial fuel saving, increase in cargo capacity and subsequent reduction of greenhouse gas emissions, improved life-cycle performance and reduced maintenance costs due to improved corrosion resistance. As the use of thermoset polymers in shipbuilding increases, so too does the interest in finding suitable alternatives to the use of petroleum-based materials. The study of bio-based resin systems and natural fibres has been a popular research topic due to the neccessity to reduce dependency on non-renewable energy/material sources, lower pollutant emissions, lower greenhouse gas emissions, enhance energy recovery, and offer end-of-life solutions for thermoset-matrix components [1]. Currently, the range of commercially available "green" composite constituents is small and not yet proven in large marine structures, which presents a hurdle for large-scale adoption of fully bio-based composites in this application. However, the combination of both petroleum- and bio-based materials to produce a structure having the requisite cost-performance properties for marine applications presents a viable solution to lower power consumption and the associated CO_2 and greenhouse gas emissions in the production of these materials in the near future [1]. To this end, much work has been published on resin systems and reinforcement fibres from natural raw materials; however, the mechanical performance of bio-based resin systems in comparison to petroleum-based equivalents with various reinforcing fibres is not widely documented.
The aim of this study is to assess the potential of using a partially bio-based resin system with synthetic and natural fibres to reduce the environmental impact of the composite material without significantly compromising the mechanical properties. This work represents a part of a selection procedure to identify the most suitable materials for large-length ship construction. Commercially available two-part epoxy resin systems (one petroleum-based and the other partially bio-based) were used to manufacture glass, carbon and basalt FRP laminates using the Vacuum assisted Resin Transfer Moulding (VaRTM) process. Mechanical properties of test coupons extracted from the laminates were assessed in relation to flexural strength and modulus, apparent interlaminar shear strength and dynamic mechanical properties under dry and wet conditions.

Experimental

Materials

The baseline epoxy (EP) used in this study was PRIME™ 27 from Gurit and the bio-epoxy (BEP) was Super Sap INR Epoxy Resin from Entropy Resins. The BEP has 19% bio-based carbon content. SuperSap formulations contain renewable plant-based carbon that replaces some of the petroleum-based carbon used in the production of the resin. The biobased components of the formulation are co-products or waste products of other industrial processes, and therefore do not compete with food sources or displace food-based agriculture to produce the resin [2]. The properties of the two resin systems according to the manufacturer's datasheet are summarized in Table 1. Three reinforcement fabrics were used to compare the performance of the EP and BEP as candidate matrix materials: glass (SAERTEX U-E-996g/m^2), basalt (Basaltex BAS UNI 350-416g/m^2) and carbon (SAERTEX U-C-314g/m^2). Basalt fibres offer some advantages as a mineral-based natural fibre for the marine industry as they are non-combustible, have reportedly comparable mechanical properties to most types of E-Glass, and are cheaper than carbon fibre [3].

Property	Prime 27	Super Sap
Density	1.08 g/cm^3	1.10 g/cm^3
Viscosity 25°C	200 mPa.s	300 mPa.s
Gel Time 25°C	2hr 40min	2 hr
Curing time 25°C	24 hr	24 hr
Post-cure temperature	60°C	120°C
Post-cure time	7 hrs	2 hrs
Glass Transition Temperature	69°C	90°C
Tensile strength	74.3 MPa	68.9 MPa
Tensile modulus	3.3 GPa	3.4 GPa
Flexural Strength	119 MPa	106 MPa
Flexural Modulus	3.2 GPa	2.6 GPa

Table 1: *EP and BEP Matrix Properties*

Manufacture

All laminates were manufactured on a glass tool using a [0°]2S stacking sequence. The Prime 27 synthetic EP was infused at ambient temperature, however the high viscosity of the BEP meant that the resin needed to be heated to 30°C to shorten infusion times. The recommended ratios of hardener from the supplier were used for each system. 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). Synthetic EP infusion times for the type of laminate shown in Figure 1 were approximately 20 minutes, while the BEP times were around 90 minutes. Curing and post-curing conditions for the materials are in accordance with the values stated in Table 1. The lay-up and the thickness of the laminates were in accordance with the relevant test methods. Test coupons were extracted using a water-cooled diamond coated rotating disc cutter.

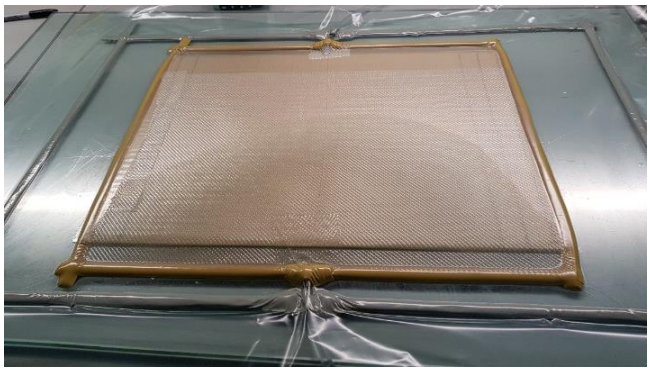

Figure 1: *Liquid Resin Infusion of glass fabric (500 mm wide x 350 mm long)*

Environmental Conditioning

Samples were dried for 4 hours at 45 °C prior to testing (dry and wet condition). Samples were immersed in distilled water at 35°C for 28 days, in line with Lloyds Register Book K, Procedure 14-1, Rev 1 Dec 2013 (wet condition only).

Physical and Mechanical Testing

Fibre Volume Fraction

Fibre content was determined using a resin burn-off method in accordance with ASTM D3171. The mass of the dry sample was recorded before and after placing the specimen in a crucible in a furnace at 550°C for two hours. This method removes the matrix and leaves behind only the dry fibres. Where this method was not suitable, e.g. in the case of charring, thickness measurements were used to determine the fibre volume fraction (FVF).

Flexure

Three-point bend tests were performed under quasi-static loading conditions in accordance with ISO14125. Nominal specimen dimsensions were 100 mm x 15 mm x 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.

Apparent Interlaminar Shear Strength

Short-span three-point bend tests were conducted under quasi-static loading conditions in accordance with ISO14130 to determine the apparent Interlaminar shear strength (ILSS). Nominal specimen dimsions were 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.

Dynamic Mechanical Thermal Analysis

Dynamic Mechanical Thermal Analysis (DMTA) was conducted using a TA Instruments Q800 Dynamic Mechanical Thermal Analyser using a three-point bend fixture in order to assess the viscoelastic properties of the material in flexure. The specimens were heated from ambient temperature to 180°C 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 all recorded during the test. The T_g is taken as the tan delta peak temperature.

Results and Discussion

Fibre Volume Fraction

The results for the FVF are shown in Table 2. It can be seen that the basalt reinforced laminates had the lowest FVF. There was no significant difference between the FVFs of the BEP and EP laminates with the same reinforcing fibres, except in the case of the glass laminates, where the glass/EP had a higher FVF than the glass/BEP laminate. Cured ply thickness (Table 2) was also measured and was shown to increase with decreasing FVF. It was observed that the cured ply thickness is not affected by the matrix, but appears to be consistent across laminates with the same reinforcing fibres. The only exception was the glass/BEP laminate.

Water Absorption

Figure 2 shows the progression of moisture uptake during the recommended 28-day immersion in water of each of the six types of samples. None of the materials exceeded the maximum amount of moisture uptake during the immersion period recommended by Lloyds Register Book K, Procedure 14-1, Rev 1 Dec 2013. The moisture mass percentage of each material in descending order is given in Table 2. The trend in moisture uptake is clear – all materials manufactutred using the synthetic EP resin absorbed significantly more moisture during the immersion period than the same reinforcement fabric infused with the BEP matrix. Basalt fibres had the highest moisture uptake with both matrices, followed by carbon and glass. Interestingly the moisture uptake increased with decreasing FVF as there was more matrix available to

contribute towards the diffusion of moisture into the material. The greater diffusivity for the carbon specimens when compared to glass can be attributed in part to the smaller fibre diameters (~7 μm) compared to glass fibres (~20 μm), which results in greater interface area per unit volume [4]. The moisture uptake for the basalt fibre reinforced materials was highest - this could be due to a combination of low FVF and poor basalt fibre/matrix adhesion meaning that the moisture can travel more easily along the fibre/matrix interface [5].

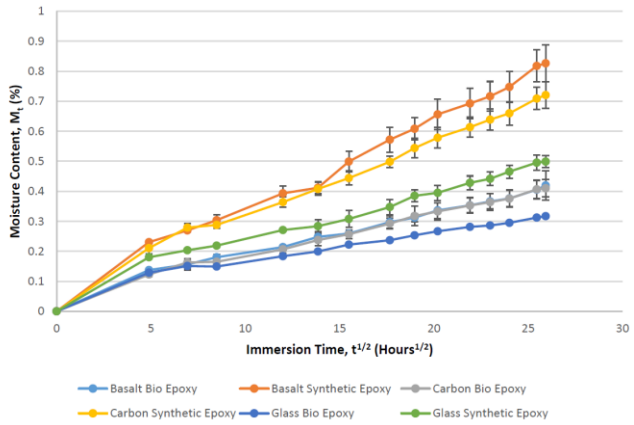

Figure 2: *Average moisture uptake of each material during the 28 days of immersion in deionised water at 35°C*

Material	Cured Ply Thickness	FVF	Moisture Uptake
Basalt / EP	0.86 mm	37%	0.83%
Carbon / EP	0.80 mm	44%	0.72%
Glass / EP	0.73 mm	54%	0.49%
Basalt / BEP	0.86 mm	37%	0.42%
Carbon / BEP	0.76 mm	45%	0.41%
Glass / BEP	0.85 mm	46%	0.32%

Table 2: *Cured ply thickness, FVF and moisture uptake after 28 days values for all materials*

Flexure

Three-point bend tests were conducted on the materials in both wet and dry conditions to determine the flexural strength and modulus. The results of the flexural strength are presented in Figure 3. In general, the EP-matrix laminates had higher (by less than 10% in all cases) flexural strengths than the BEP-matrix laminates. This was more pronounced in the basalt fibre laminates than in the glass and carbon. The superior performance of the EP in comparison to the BEP is expected, however, the performance of the BEP laminates meets the minimum requirements as stated in Lloyds Register Book K, Procedure 14-1, Rev 1 Dec 2013. This indicates that the bio-based resin system can be a potential candidate for material selection for large-length ship design. The reduction in flexural strength due to the presence of moisture in the composite material is relatively small for all material systems with the BEP laminates having the smallest drop in properties, due to the lower moisture uptake levels during the immersion period. The largest drop in properties due to the presence of moisture was observed in the basalt/EP laminate – this was also the material with the highest moisture content. Figure 4 and Figure 5 show the dry and wet failure locations of the EP-matrix and BEP-matrix flexure samples, respectively. It can be seen that there is no major modification to the failure mechanism due to the presence of moisture. However, the basalt/EP and glass/BEP samples show a slightly more significant global failure in the wet state than in the dry state. These samples had the largest drops in flexural strength due to the presence of moisture – both had significant reductions of 17% while the other four systems had reductions in flexural strength due to moisture of less than 3%.

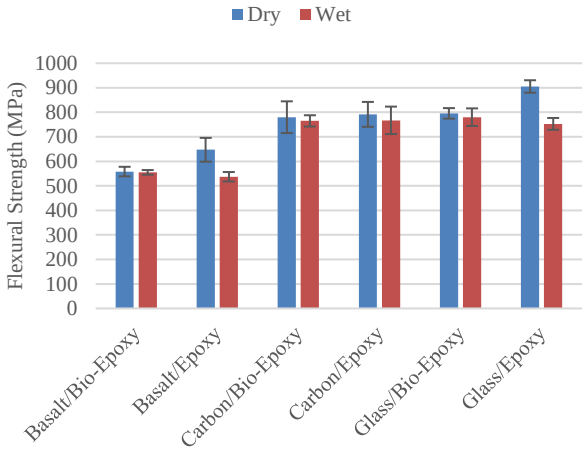

Figure 3: *Flexural strength values for all materials tested under dry and wet conditions*

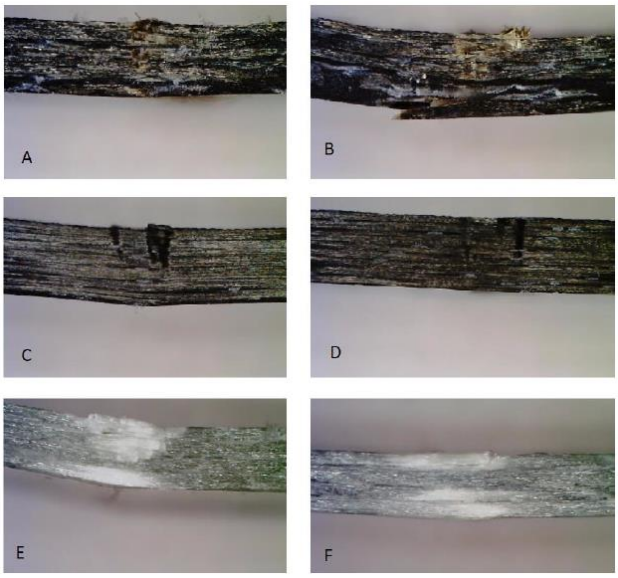

Figure 4: *Images of failure of flexure samples basalt/EP (a) dry and (b) wet, carbon/EP (c) dry and (d) wet, glass/EP (e) dry and (f) wet. Nominal thickness of specimens is 3 mm.*

Figure 6 shows the results of the flexural modulus values for all materials. The carbon/EP and carbon/BEP samples had the highest flexural modulus due to the high longitudinal modulus of the reinforcement fibres.

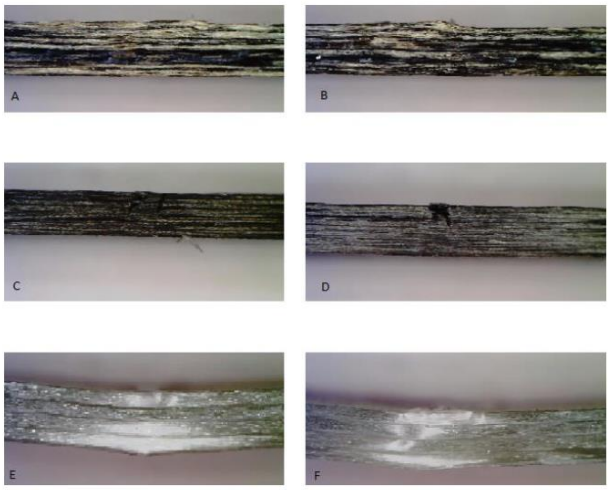

Figure 5: *Images of failure of flexure samples basalt/BEP (a) dry and (b) wet, carbon/BEP (c) dry and (d) wet, glass/BEP (e) dry and (f) wet. Nominal thickness of specimens is 3 mm*

There is no significant difference in the flexural modulus of the EP and BEP basalt and carbon laminates (less than 4%), however, the glass/EP has a modulus 23% higher than the glass/BEP. According to Table 1, the modulus of the EP resin is almost 20% higher than that of the BEP, so the performance of the BEP as a composite matrix is actually in line with what would be expected when used with the glass fibres, and exceeds the expected modulus when used with the basalt and carbon fibres. This illustrates the potential of BEP to be a candidate material for marine structures with the added benefit of reduced carbon footprint associated with the material production.

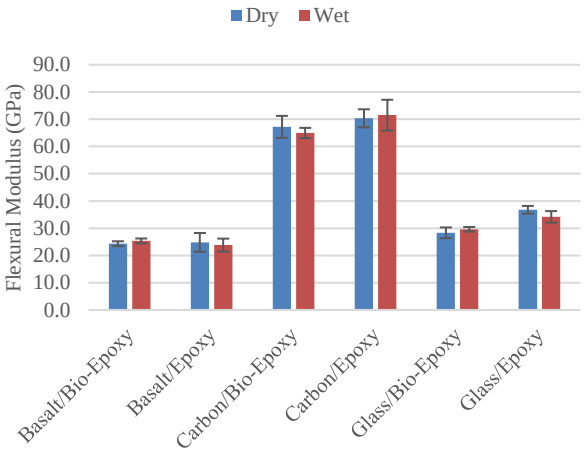

Figure 6: *Flexural modulus values for all materials tested under dry and wet conditions*

Apparent Interlaminar Shear Strength

Figure 7 shows the apparent ILSS of the dry and wet specimens tested using the short beam shear test method. The lowest values are observed in the basalt laminates, specifically with the BEP matrix (27% lower than its synthetic counterpart). This low performance could be potentially attributed to poor fibre/matrix interfacial strength. For carbon laminates, there is little difference in the ILSS values for the BEP and EP matrices (within 1%), while the glass/BEP ILSS is 11% higher than the glass/EP ILSS. There was relatively little decline in the ILSS due to the presence of moisture after the immersion period (less than 7% in all cases). The water molecules are known to degrade the fibre/matrix interface, which influences the ILSS of the material, hence it is positive that the reduction in this property due to the presence of moisture was small. The materials still exceed the minimum ILSS requirements according to Lloyds Register Book K, Procedure 14-1, Rev 1 Dec 2013 even after the recommended immersion period. Figure 8 shows an image of the typical failure observed in all ILS specimens – the failure in the samples occurred as a delamination along the mid-plane and was concentrated in one half of the specimen.

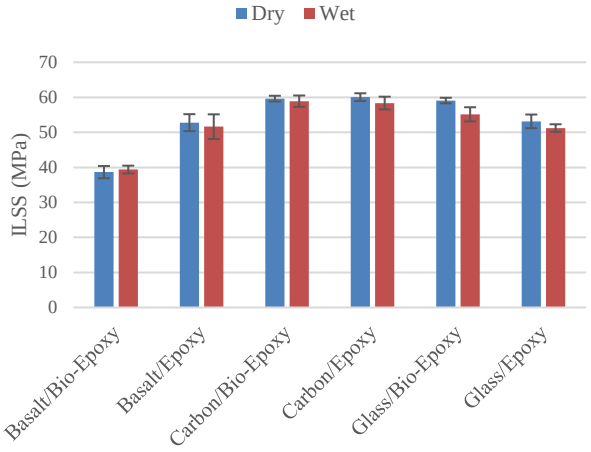

Figure 7: *ILSS values for all materials tested under dry and wet conditions*

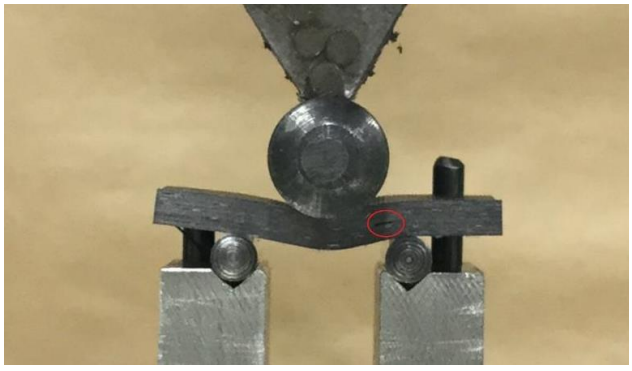

Figure 8: *Carbon ILS coupon showing interlaminar failure limited to one side at the mid-plane.*

Dynamic Mechanical Thermal Analysis

During this study, DMTA testing 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. Table 3 shows the onset temperature (the temperature at which the storage modulus decreases dramatically) and the glass transition temperature (T_g) which was taken as the temperature corresponding to the peak in the tan delta curve. The BEP laminates have significantly higher onset and T_g values than the EP laminates. As evident from Table 3, the type of reinforcement fibre does not a have a significant influence on the temperatures reported.

Material	Onset (°C)	T_g (°C)
Basalt/EP	76.0	86.5
Carbon/EP	76.0	85.5
Glass/EP	74.5	86.2
Basalt/BEP	98.1	112.2
Carbon/BEP	97.0	109.5
Glass/BEP	100.7	114.0

Table 3:*EP- and BEP-composite onset temperature and T_g*

Summary

The aim of this study was to assess the potential of using a partially bio-based epoxy resin system with synthetic and mineral-based natural fibres to reduce the environmental impact of the composite material without significantly compromising the mechanical properties. The key findings of this study are:

- In contrast to the petroleum based epoxy, elevated temperature (30°C) was required to infuse the BEP for all reinforcements; this is an important consideration for the infusion of large structures. DMTA showed that all laminates were tested in a fully cured state. As expected from the data sheets, T_g and Onset temperatures were higher in the BEP samples than the EP.
- In the dry condition, the flexural strength of the BEP laminates was within 10% of the EP laminates. Only the basalt/BEP laminates showed a greater knockdown (14%) in strength while only the glass/BEP laminates exhibited a large knockdown (23%) in flexural modulus.
- In the dry condition, the ILSS of the bio-based samples was almost identical to the petroleum-based samples (within 1%) in the case of the carbon-reinforced samples, while the glass/BEP ILSS was 11% higher than the glass/EP. However, the basalt/BEP ILSS was 27% lower than the basalt/EP.
- Moisture absorption results showed that the BEP laminates had lower moisture uptake than the EP laminates. Moisture uptake resulted in minor degradation (less than 7%) of ILSS in both the BEP and EP laminates. Regarding the effect of moisture on flexural strength, only the glass/EP and basalt/EP samples showed a significant reduction (17%) due to the presence of moisture. The properties of all BEP laminates were unaffectedby the presence of moisture
- Regarding the effect of reinforcement, the glass laminates performed similar to the carbon laminates in term of flexural strength in all conditions. Basalt laminates did not perform as well possibly due to the low FVF. Regrading ILSS, carbon laminates performed best followed by the glass/BEP. The basalt/EP performed similar to the glass/EP laminate, but the ILSS of basalt/BEP was significantly lower.

Overall, the BEP compared well with the EP as a composite matrix and has potential for future use in large marine structural applications; however, the higher viscosity of the BEP and the corresponding issues with infusion times can be important considerations for infusion manufacture of large marine structures.

Acknowledgment

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