DEVELOPMENT OF HIGH PERFORMANCE BIO-COMPOSITES BASED ON FURAN BIO-RESINS FOR VEHICLE PANELS

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ABSTRACT

Composite materials derived from renewable, sustainable sources have received significant interest in recent years due to the depletion of the earth's resources and the incessant rise in the price of oil. Natural fibres, such as hemp, flax, jute and kenaf, are already used in significant quantities to reinforce conventional polymers, although the fibres tend to be short and randomly oriented so mechanical performance is limited. A number of bio-derived resins are under development but are not yet ready for commercial application. These shortfalls are being addressed by a European Sixth Framework Programme Project called *BIOCOMP*, which aims to develop high-performance composite materials made entirely from renewable resources. As part of this project, novel furan thermoset resins derived from furfuryl alcohol have been developed, suitable for use in traditional composite manufacturing processes. These furan resins have high temperature stability, good fire resistance and excellent chemical resistance, and are a potential sustainable alternative to epoxy or phenolic resin systems. In addition, quasi-continuous, aligned natural fibre reinforcements have been obtained by using low-twist natural fibre yarns and fabrics. Test panels have been produced from glass fibre-reinforced furan resin using hand lay-up and vacuum bagging processes, and from aligned flax fibre-reinforced furan resin using a prepreg technique with vacuum and press consolidation. These panels have been subjected to a range of mechanical and physical tests and the results compared to conventional composite materials such as glass fibre-reinforced unsaturated polyester. The bio-based material exhibited some promising characteristics. Prototype vehicle panels have been produced from flax fibre-reinforced furan, glass fibre reinforced-furan and glass fibre-reinforced unsaturated polyester and these have been evaluated and compared to the performance requirements.

1. INTRODUCTION

The use of fibre-reinforced plastic composites in the automotive industry has grown significantly in recent years due to their low weight, design flexibility, corrosion resistance and cost-effectiveness, in particular for low volume, niche vehicles. Glass fibre is commonly used as the reinforcement, often in the form of random, chopped strand mats and unsaturated polyester resin is a popular matrix polymer. Hand lay up, resin transfer moulding and vacuum infusion are all well established processing techniques, well suited to the manufacture of composite vehicle parts, such as exterior and interior panels.

Currently, there is a significant drive to switch to more sustainable and renewable materials, whilst reducing weight and cost. For example, density and cost can be reduced by replacing glass fibre with natural fibres such as hemp, flax or kenaf [1-2]. The specific stiffness, which is the stiffness as a function of density, of natural fibres exceeds that of glass fibres [3].

Natural fibre composites have found applications in the automotive industry, although these are largely for non-structural parts such as interior panels. This is partly due to the composites being manufactured from short, non-woven fibre mats [4], which leads to products that have limited mechanical properties. In addition, the natural fibres are generally used with conventional resins such as unsaturated polyester and polypropylene [5-6], meaning that only the fibres are from renewable sources.

Thermoplastic bio-resins such as polylactic acid (PLA), polyhydroxybutyrate (PHB) and starch-based polymers are currently being developed and used primarily for food packaging [7]. Much of their appeal in the packaging industry lies in their biodegradable nature. Some thermosetting bio-resins derived from plant oils such as soybean [8-9] and linseed [10] are currently under development but are not ready for commercial application.

New classes of engineering composite materials from renewable resources are being developed and commercialised through *BIOCOMP*, an Integrated Project for SMEs supported by the European Commission through the Sixth Framework Programme (FP6). A primary objective of the *BIOCOMP* project is to develop high-performance composite materials entirely derived from renewable sources using a new family of furan-based resins reinforced with continuous, aligned natural fibres.

The furan-based resins are being developed by TransFurans Chemicals under the trade-names BioRez™ and Furolite™. The resins are synthesized from pre-polymers of furfuryl alcohol, which is derived from biomass sources including sugar cane bagasse (Figure 1). Furan resins offer a number of interesting properties such as high stiffness, fire resistance and chemical resistance to organic and inorganic acids.

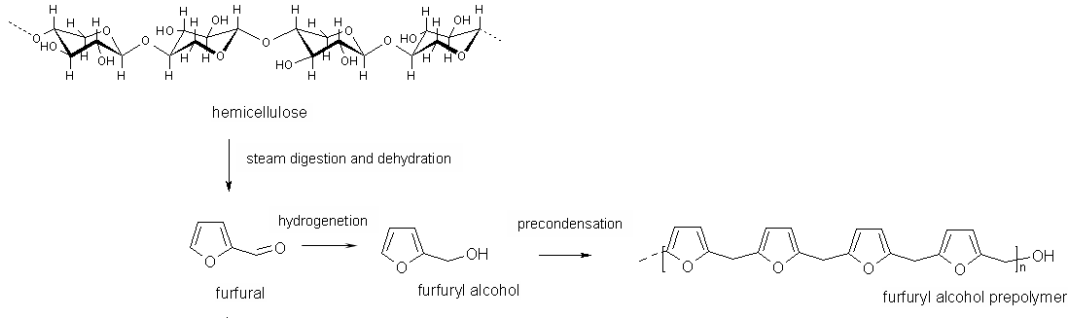


Figure 1: Production route of furfuryl alcohol prepolymer resin from hemicellulosic biomass.

This paper discusses work undertaken during the *BIOCOMP* project to develop high-performance furan-based bio-composites for a range of applications, including automotive parts, based on furan-based resins are being developed by TransFurans Chemicals. An external panel from a low-volume utility vehicle was used to demonstrate and evaluate the materials against a specification. NetComposites Ltd. developed the manufacturing process and produced test samples and prototype panels and MERL Ltd. conducted all the evaluation tests. Typical requirements for this type of component include mechanical integrity, impact resistance, environmental resistance, good surface finish, acceptable cost at low production volumes (*e.g.* 200/year).

2. MATERIALS AND PROCESSING

Two grades of furan resin have been investigated in this study: *(1)* a 2-part, low viscosity resin suitable for use with glass fibres and *(2)* a 1-part prepreg system for use with natural fibres. The 2-part resin includes an acid-based catalyst, added at 6 wt%, which was found to degrade the natural fibres during initial tests. A pH neutral resin was therefore developed for use with natural fibres. Due to the higher viscosity of this modified resin, the resin had to be dissolved in a solvent in order to impregnate the fibres properly. After impregnation, the solvent was evaporated off leaving a furan-flax prepreg containing 40 wt% fibres.

Standard Glass fibre reinforced polyester (GRP) materials were manufactured and tested for benchmark comparison purposes, using an unsaturated polyester resin, namely Crystic 489PA from Scott Bader Ltd., with 2 wt% MEKP catalyst.

A powder bound glass fibre chopped strand mat (CSM) 450gsm was used as the reinforcement in the furan-glass system. An emulsion bound glass fibre chopped strand mat 450gsm was used as the reinforcement in the polyester-glass system. A unidirectional flax stitched fabric with cotton stitch yarn was used in the prepreg. The fabric (230gsm) was made from loosely twisted yarns in order to improve resin impregnation and to maintain fibre alignment.

Both flat test panels and prototype vehicle panels were produced from furan-glass, polyester-glass and furan-flax. The vehicle panel tool was a single cavity epoxy board mould.

2.1 Glass fibre/Furan (BioCompA)

Four layers of 450gsm glass CSM and the 2-part furan resin were laid up into the prepared mould using brushes and rollers. Being a development system, the furan resin was not formulated to include thixotropic or low-shrink additives. Therefore, following lamination, the parts were vacuum bagged and a vacuum of 0.9 bar was applied to the system during curing to improve part quality. This also resulted in a part with higher fibre volume fractions than a standard hand lay-up part (32 wt% resin). The parts were cured at room temperature for 140 min, 50 °C for 45 min and 80 °C for 45 min, and then post-cured at 80 °C overnight (approximately 18 hrs).

Figure 2: Prototype furan-glass fibre exterior vehicle panel.

2.2 Glass fibre/Polyester (GRP)

Four layers of glass CSM and polyester resin were laminated into the mould as above, vacuum bagged and cured overnight at room temperature (approximately 18 hrs), followed by a 3 hour post-cure at 80 °C.

2.3 Flax fibre/Furan (BioCompB)

Four layers of furan-flax prepreg were laid into the prepared mould in a balanced cross-ply lay up $[0/90]_S$. A vacuum bag was applied to the system and the part was cured in an oven for 15 minutes at 150 °C. Approximately 20% by weight resin was lost through resin bleeding, resulting in parts with final fibre content of approximately 60 wt% and higher levels of porosity than desirable. Further development is required to reduce the resin bleeding.

3. EXPERIMENTAL PROCEDURES

A comprehensive experimental programme was set-up in order to characterize the behaviour of the three materials considered in this work. Mechanical and physical tests were performed to assess some key elements of the behaviour of the materials and these are presented in detail in the following sections.

3.1 Exposure to fluids

A utility vehicle panel will be exposed to a number of fluids and environments while in service. Therefore, a number of tests were performed to investigate the behaviour of the materials when exposed to these fluids. Flat, square 50 × 50 mm test pieces, were cut from the manufactured panels and immersed in the following fluids: *(1)* Motor oil 10W30 *(2)* Hydraulic oil 10W40 *(3)* Diesel oil *(4)* Antifreeze fluid (ethylene glycol 99%) *(5)* Windscreen wash *(6)* Pesticide and *(7)* Distilled water. In parallel to mass change, Barcol hardness was also measured for the GRP and the BioCompA materials. However, due to the very high surface roughness, Barcol hardness could not be measured for the BioCompB. All immersions took place at ambient laboratory conditions (23±2 °C, 55±5 % RH) with test pieces being weighed at regular intervals. Samples were immersed for a period of up to 2,000 hrs. Water immersion of GRP and BioCompA lasted for approximately 3,600 hrs.

Apart from the square samples, dumbbell shaped tensile test pieces were also immersed in all seven fluids in order to assess the effect the fluid uptake (saturation level) on the basic mechanical properties. A number of samples for fastener pull through and impact resistance tests were immersed in water over a period of time and their response was also assessed and compared to that of un-aged samples.

3.2 Tensile tests

Tensile tests were performed following the ISO 527-4 International Standard [11]. Dumbbell shaped test pieces (specimen type 1B) were machined from the manufactured flat panels using a CNC facility. All tests were performed on a ZWICK Z250 test frame, using a 5 kN load cell and a crosshead speed of 5 mm/min. Tensile tests were performed on un-aged (as received) samples as well as on samples exposed for a certain period of time to a number of fluids, as described above.

3.3 Fastener pull through tests

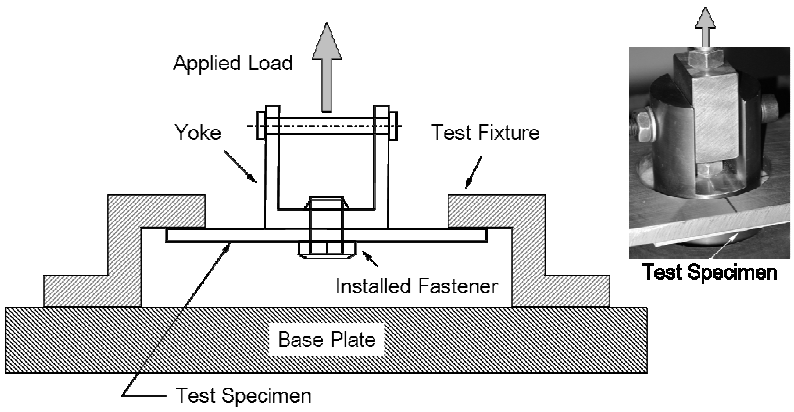


Figure 3: Experimental set-up details for fastener pull through tests.

Since the installation of the prototype utility vehicle panel will involve the use of a number of fasteners, the fastener pull through response of the materials was investigated. For the experimental work ASTM D7332 [12] Standard was adopted. Flat, 108 × 108 mm test specimens were cut from the panels. A 10 mm clearance hole was drilled at the centre of the test piece and an M10 fastener installed. The experimental set-up for the test can be seen in Figure 3. All tests were performed at ambient laboratory conditions, utilizing a ZWICK test frame and using a 5 kN load cell. Loading was applied at a rate of 5 mm/min. Tests were performed prior and after immersion in distilled water to assess the durability of the materials.

3.4 Impact tests

One of the main in-service threats for a utility vehicle panel is impact due to road debris, vandalism, *etc*. Thus, impact resistance was investigated for all the materials. Drop weight impact tests were performed on rectangular 150 × 100 mm flat test specimens cut from the manufactured panels. Different impact energy (impact velocity) levels were achieved by altering the drop height (0.3 to 1.2 m) of the 2.5 kg impactor mass. A hemispherical impactor nose, 10 mm in diameter, was used for all tests. A load cell attached to the impactor was used to measure the impact response of the materials. Test specimens were clamped at four corners using toggle clamps on top of a 125 × 75 mm window frame. The experimental set-up can be seen in Figure 4.

Due to the large difference in thickness (BioCompB panels had a nominal thickness of 2 mm while GRP and BioCompA ones 4 mm), different impact energy levels were applied to the samples but the ratio of impact energy per unit thickness of the material was kept constant. Tests were performed on dry (as received) samples as well as on samples saturated with water.

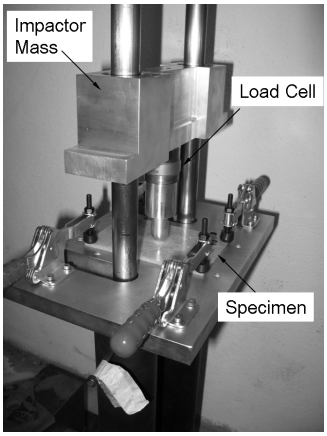


Figure 4: Drop weight impact test set-up.

4. EXPERIMENTAL RESULTS

4.1 Exposure to fluids

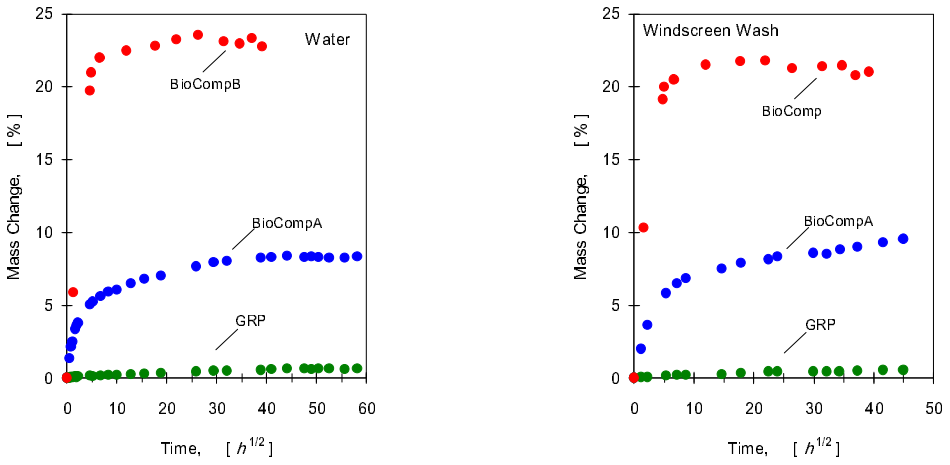
Results of the fluid exposure tests are given in Table 1. The mass at equilibrium (saturation level) is used as a means to quantify the effect of the various fluids on the three materials under investigation.

GRP fluid absorption levels were found to be very low and in all cases significantly lower than BioCompA and BioCompB. In one case (immersion in anti-freeze) GRP

samples showed an early maximum followed by a continuous decrease in weight until they reached equilibrium at a weight lower than the initial one. That indicated significant leaching of constituents in the anti-freeze fluid. Both BioCompA and BioCompB samples absorbed a considerable amount of the fluids, with BioCompB reaching 23.2% increase in weight following immersion in water. The fluid absorption behaviour has Fickian characteristics for water and windscreen wash (Figure 5(a) and (b)). The considerable difference between BioCompA and BioCompB indicated that the flax fibres also absorb a great amount of fluids during immersion. The initial furan-flax materials (BioCompB) had higher porosity than ideal, which may have contributed to the relatively high fluid uptake results. The fluid immersion was found to have an effect on the surface characteristics of the GRP and BioCompA samples, which leaded to a decrease in Barcol hardness.

Table 1: Fluid mass uptake and Barcol Hardness test results

	Mass Change, M_∞ [%]		
Material	GRP	BioCompA	BioCompB
Motor Oil 10w30	0.2	1.1	14.5
Hydraulic Oil 10w40	-	1.3	13.2
Diesel	-	1.7	10.4
Anti-freeze	-0.1	8.3	18.0
Pesticide	0.7	8.7	22.2
Windscreen wash	0.5	9.6	21.2
Distilled Water	0.6	8.3	23.2
All results for up to 2,000 hrs immersion except GRP and BioCompA in water that correspond to 3,600 hrs			



(a) (b)

Figure 5: Plots of the mass change of the three materials immersed in (a) water and (b) windscreen wash.

4.2 Tensile tests

Some basic mechanical data for the three materials are summarized in Table 2 as measured from uni-axial tensile tests. Young's modulus was found to be very similar for the three materials. However ultimate tensile strength and strain to failure was considerably different. BioCompB was found to have the lowest strain to failure and

tensile strength. The structure of the reinforcement material (biaxial *vs.* random oriented fibres) will play a significant role in the tensile response. The properties of the three materials under consideration before and after immersion in various fluids are summarized in Table 3.

Table 2: Mechanical properties of the materials tested (Mean Values ± Stdev)

Material	Tensile Strength MPa	Young's Modulus GPa	Strain to Failure %
GRP	131±27	9.2±1.1	1.6±0.2
BioCompA	93±8	7.2±1.0	2.3±0.3
BioCompB $[0/90]_S$	64±9.5	8.5±0.8	0.9±0.1

Table 3: Tensile strength and Young's modulus of GRP, BioCompA and BioCompB after immersion in various fluids

Material	GRP		BioCompA		BioCompB $[0/90]_S$	
	Tensile Strength MPa	Young's Modulus GPa	Tensile Strength MPa	Young's Modulus GPa	Tensile Strength MPa	Young's Modulus GPa
Before immersion	131±27	9.2±1.1	93±8	7.2±1.0	64±9.5	8.5±0.8
Motor Oil 10w30	96±7.0	7.7±0.4	86±7.0	6.6±0.3	64±6.0	8.5±0.7
Hydraulic Oil 10w40	98±9.5	8.1±0.5	91±7.5	6.7±0.4	53±5.5	7.4±0.6
Diesel	99±11.0	7.9±0.1	89±8.0	6.7±0.4	55±4.5	7.5±0.5
Anti-freeze	101±8.0	8.5±0.6	89±12.0	6.4±0.6	56±9.5	4.7±0.4
Pesticide	94±3.0	8.0±0.5	79±4.0	5.2±0.3	61±8.0	3.3±0.3
Windscreen wash	95±9.0	7.4±0.1	80±6.0	5.1±0.4	65±4.0	3.4±0.1
Distilled Water	99±1.0	7.7±0.2	85±5.5	5.7±0.4	61±4.5	3.2±0.1

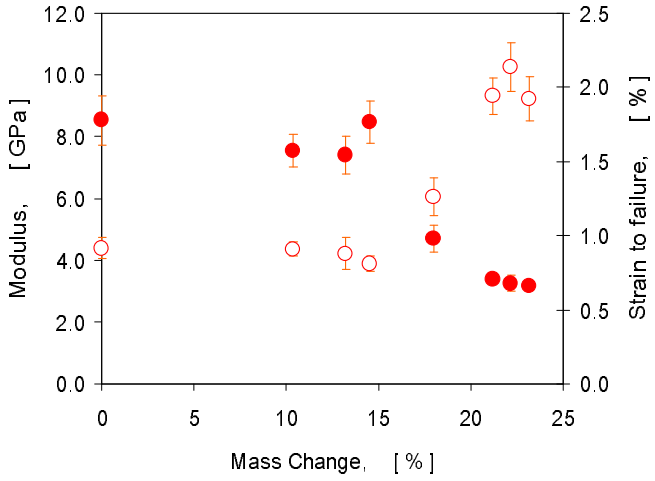


Figure 6: Variation of modulus and strain to failure with mass change during immersion in various fluids for BioCompB.

Stiffness of the GRP material appears to be slightly reduced by the immersion in the various fluids and the decrease in modulus was found to be approximately the same for all fluids. Tensile strength was reduced to a greater extent but again similar results were obtained for all fluids. BioCompA followed a similar trend and only pesticide, windscreen wash and water caused a more noticeable drop in strength and modulus.

The effect of fluid exposure is more evident in the mechanical behaviour of BioCompB. Large fluid uptakes (pesticide, windscreen wash and water) resulted in a more ductile material with considerable loss in stiffness (Figure 6).

4.3 Fastener pull through and bearing strength tests

The experimental results of the fastener pull through tests, prior to (un-aged) and after water immersion are presented in Figure 7. Photographs of some characteristic samples after testing are presented in Figure 8.

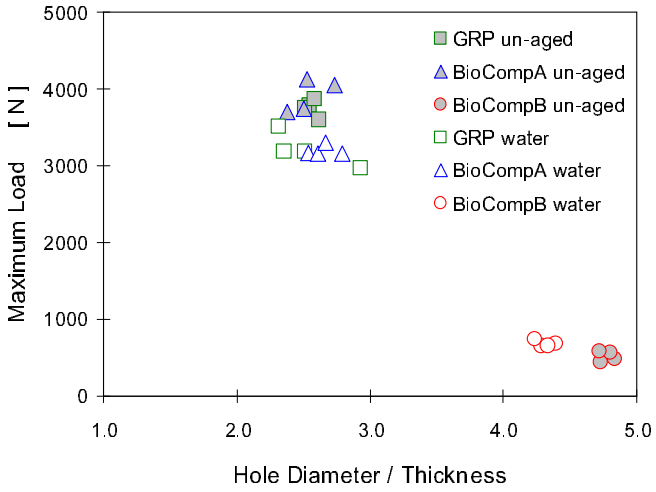


Figure 7: Experimental maximum pull through load plotted as a function of the hole diameter to thickness ratio for each sample.

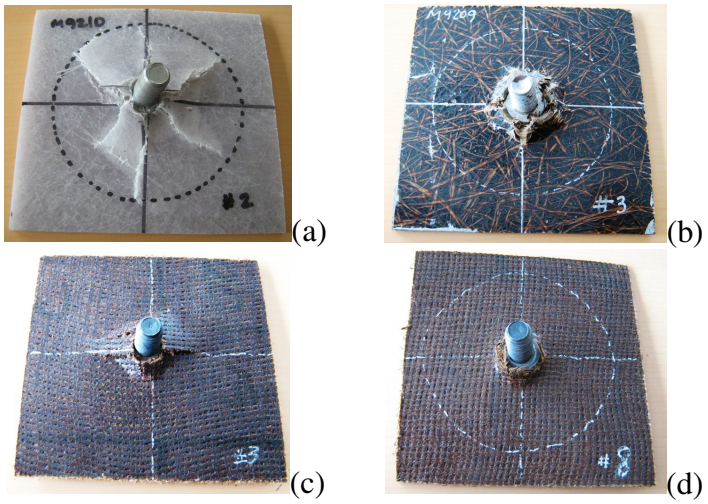


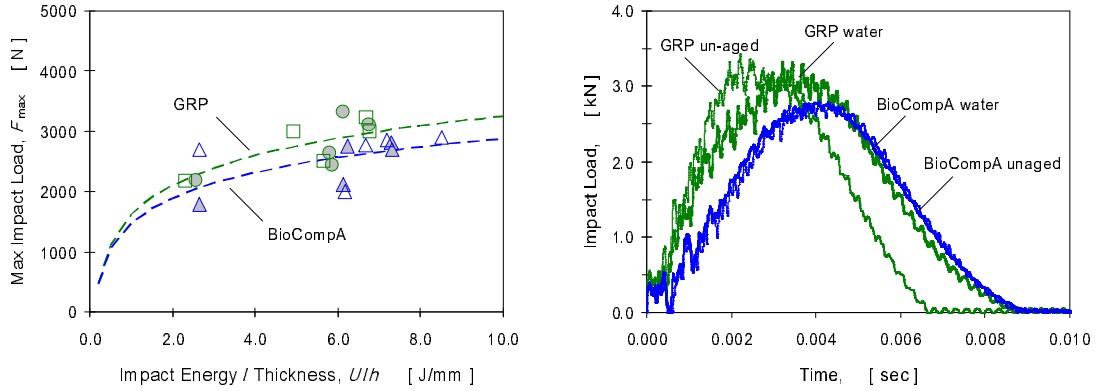
Figure 8: Photographs of the fastener pull through failure mode of the three materials; (a) GRP un-aged (b) BioCompA un-aged (c) BioCompB un-aged and (d) BioCompB water immersed samples.

The results indicated no significant difference between the GRP and BioCompA in terms of maximum pull through load. However, the mode of failure for the two materials was majorly different. GRP samples showed a bending type failure, with cracks initiating around the fastener and propagating towards the support of the sample, while BioCompA samples presented a pure pull thought failure mode (Figure 8(a) and (b)). After water immersion there was a slight drop in the maximum pull load but no

apparent change in the mode of failure. BioCompB was found to have fairly poor pull through strength. The un-aged samples behaved in a brittle manner and a bending type failure occurred at an average maximum load of 520 N. After water immersion the behaviour of the material was evidently more ductile (higher displacements to failure) and the average maximum load increased up to 680 N. The failure mode in this case was also different (Figure 8(d)). The decrease in the fastener hole diameter to thickness ratio is due to the increase in thickness of the water immersed samples.

4.4 Impact tests

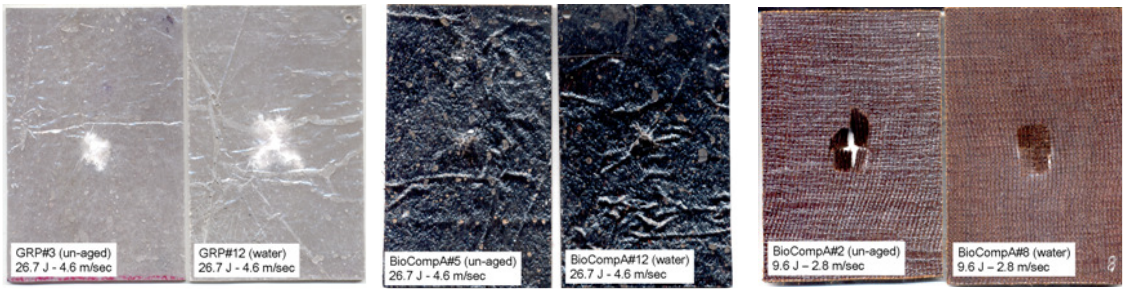
The experimental results for the drop weight impact tests are summarised in Figure 9(a). The maximum impact force was used to assess the impact response of the materials, prior and after water immersion. For similar energies (per unit thickness) the GRP samples showed marginally higher impact forces than the BioCompA samples. The maximum impact force was not found to be affected by the water immersion.



(a) (b)

Figure 9: (a) Variation of maximum impact load with normalized impact energy and (b) Force-time history for GRP and BioCompA before and after water immersion.

However, it was found that water immersed GRP samples showed higher impact duration than the un-aged ones (Figure 9(b)). That indicates higher levels of impact damage for these samples (for the same energy level), Figure 10(a). This was not observed for the case of the BioCompA samples. In general, for these two materials some local indentation at the front side was found at high energy levels, while significant fibre fracture occurred at the back side (Figure 10(a) and (b)).



(a) (b) (c)

Figure 10: Photographs of the impact induced damage on the three materials; (a) back side damage of GRP (b) back side damage of BioCompA and (c) front side damage of BioCompB samples.

In the case of BioCompB samples, perforation occurred even at very low energy levels. The failure was found to be brittle and the impact forces very low. The water immersed samples showed similar impact behaviour with evidence of less brittle failure than the dry ones. Possible plasticization of the materials due to the presence of water, as also found from the tensile and pull through tests, could result in the observed behaviour.

5. CONCLUSIONS

There is great potential in using composites made of sustainable and renewable materials. In the present study the mechanical and physical behaviour of materials under development (glass fibre/furan and flax fibre/furan) was investigated and compared to a glass fibre/polyester benchmark system. The requirements (strength, stiffness, impact resistance, chemical resistance, *etc*) were set by the potential use of these materials to manufacture utility vehicle panels. The glass fibre/furan resin system could be a good alternative to the glass fibre/polyester system. Further development is needed for the case of the fully renewable system (flax fibre/furan resin) in order to achieve the desired results.

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