Annex 2 (Feasibility Study Report)

Manufacturing Thermoplastic Fibre Metal Laminates by the In-Situ Polymerisation Route

Fibre metal hybrid laminates (FMLs), where thin metal sheets and fibre-reinforced composites are integrated, offer superior characteristics of the composites combined with the ductility of the metal phase. Hybrid composites containing continuous fibre-reinforced plies and metal layers offer unique mechanical properties. In the present investigation, infusible liquid thermoplastic (TP) resin Elium®, glass fibre reinforcements and metal sheets (Al alloy) (6082-T6) have been used to fabricate low-cost FMLs by a resin infusion method at room temperature. Since the interfacial bonding between the metal and the thermoplastic composite (TPC) layer plays a vital role in the performance of the FML, different surface treatments have been explored as a means of enhancing the interfacial bonding with the TPC layer.

This project involves three major steps:

i. To prepare the surface of the metal sheets with suitable chemical or physical treatments to achieve an acceptable level of interfacial bonding with the TPC.
ii. To manufacture FMLs using the vacuum assisted resin infusion route.
iii. To investigate the mechanical properties of the FMLs in comparison to an equivalent Elium® based reference laminate (FRP) with no metal interlayer.

Results/Deliverables

- **Surface characterisations**

Surface activation of Al alloy sheets (6082-T6) was achieved by: alkali etching with sodium hydroxide (NaOH) solution; acid etching with phosphoric acid (H_3PO_4); and atmospheric plasma [1]. A parametric investigation was conducted to determine the suitable treatment conditions for all the non-standardised methods i.e. alkali and acid etching, and atmospheric plasma. For the alkali and acid treatments, various durations (2-20 minutes) and two concentrations (10% wt. and 15% wt.) were investigated. The variable parameters for the atmospheric plasma treatments were the scan speed (1-4 mm/s) and the number of scans when the source-to-substrate distance was fixed at 0.5 mm for all trials. The lab model atmospheric plasma unit used in this study is shown below in Fig. 1.

Fig 1: Cirrus, single nozzle atmospheric plasma system from Henniker Plasma.

Surface roughness, contact angle (CA), surface energy (γ_{SV}) and work of adhesion (W_A) were evaluated for all the treated Al coupons using the aforementioned parameters, along with the degreased, as-received Al coupons and the results obtained are presented in Table 1. The wettability of the Al surfaces was studied by calculating the work of adhesion and the surface free energy values via Young's and Neumann's equations [2-3]. Typical optical micrographs of the Al surfaces (for the down-selected treatment cases) are shown in Fig. 2 and corresponding surface characteristics are presented in Table 1.

Table 1: Measurements of contact angle (CA), surface free energy γ_{SV}, work of adhesion (W_A) and surface roughness, for the different surface treatments (±standard deviation).

Al treatment	CA (º)	γ_{SV} (mJ/m^2)	W_A (mJ)	Roughness (µm)
Degreased-only Al	85 ± 1	31.1	76.6	0.416
5 min Alkali (10% wt.)	38 ± 1	60.4	130.1	0.467
10 min Alkali (10% wt.)	47± 1	55.5	122.4	0.595
20 min Alkali (10% wt.)	70 ± 2	41.7	97.7	0.835
5 min Alkali (15% wt.)	71 ± 3.5	41.1	96.5	0.551
10 min Alkali (15% wt.)	59 ± 2	48.4	110.3	0.635
20 min Alkali (15% wt.)	62 ± 2	46.6	106.9	0.813
2 min Acid	38 ± 2.5	60.5	130.2	0.376
5 min Acid	37 ± 3	61	130.9	0.408
10 min Acid	59 ± 3	48.4	110.3	0.416
20 min Acid	55 ± 3	50.8	114.5	0.424
20min Alkaline (10% wt.) + 20 min Acid	61 ± 3.5	47.2	108.1	0.920
20 min Acid + 20min Alkaline (10% wt.)	51 ± 3	53.2	118.6	0.702
Plasma (1mm/s and 1 scan)	32 ± 2	63.5	134.5	0.434
Plasma (2mm/s and 1 scan)	35 ± 2	62	132.4	0.421
Plasma (4mm/s and 1 scan)	49 ± 3	53	118.2	0.430
Plasma (1mm/s and 3 scans)	50 ± 2	53.5	119.1	0.411
Plasma (2mm/s and 3 scans)	45± 2	56.3	123.7	0.418

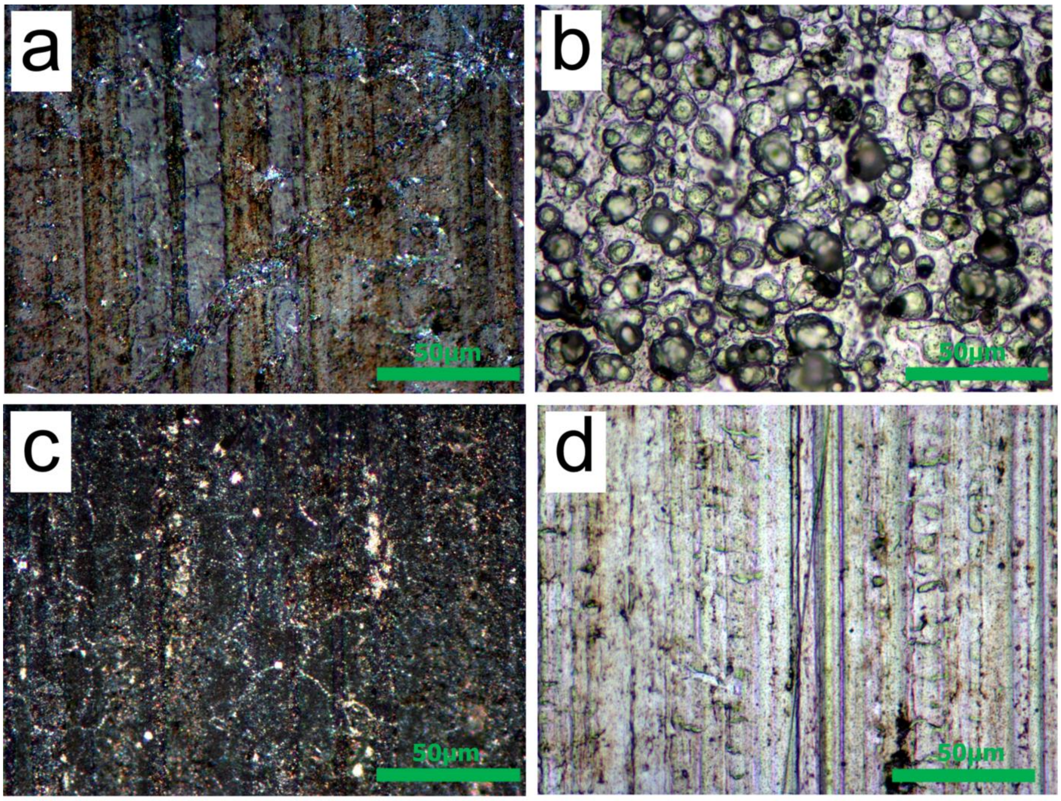

Fig 2: Typical micrographs of the treated Al surfaces under various surface treatment conditions (a) degreased (b) alkali (20 min and 10% wt.) (c) acid (10min) and (d) atmospheric plasma (2mm/s, 1scan).

- **Fabrication and testing of thermoplastic fibre-metal laminates (TPC-FMLs)**

Progress to date

- Based on the surface characterisation values, the following surface treatments were selected for use in FMLs:
  a)10% NaOH treatment for 20 min.
  b) Atmospheric plasma treatment (2 mm/s scan speed, 1 scan and source(nozzle)-to-substrate distance 0.5 mm, pressure at 6 bars, power fixed at 300W and radio frequency at 40 KHz, supplied by Henniker Plasma Company).
  c) Anodisation from external agency (sulphuric acid anodisation, according to Defence Standard 03-25)
- The surface treated Al sheets were immediately coated with a thin layer (few microns) of epoxy acrylate [4], which acted as an adhesion promoter to enhance the metal-TPC bonding through in-situ polymerisation during the composite manufacturing. This step is critical to achieve the acceptable level of bonding. The optimisation of the coating thickness or coating technique could not be done within this limited time period. This step will be thoroughly investigated in the core project.
- Laminates were manufactured successfully using a conventional room temperature vacuum-assisted resin transfer moulding (VARTM) technique, shown in Fig 3 (a). Down-selection of the optimum metal treatment method for the production of the test FMLs was performed by means of qualitative bond strength testing. Alkali etching, as per the aforementioned parameters, was found to provide the best bonding by visual inspections.
- Following the successful VARTM manufacturing of the FMLs and extraction of the test coupons with CNC (Fig 3b), preliminary mechanical characterisations were performed.

Flexural tests and short beam shear tests (for interlaminar shear strength or ILSS) were conducted on FMLs with alkali treated metal interlayer in accordance with ASTM D7264 and BS EN ISO 14125, respectively. The results obtained for the flexural tests are presented in Table 2. ILSS results are shown in Table 3 in comparison to various FML cases as reported in literature.

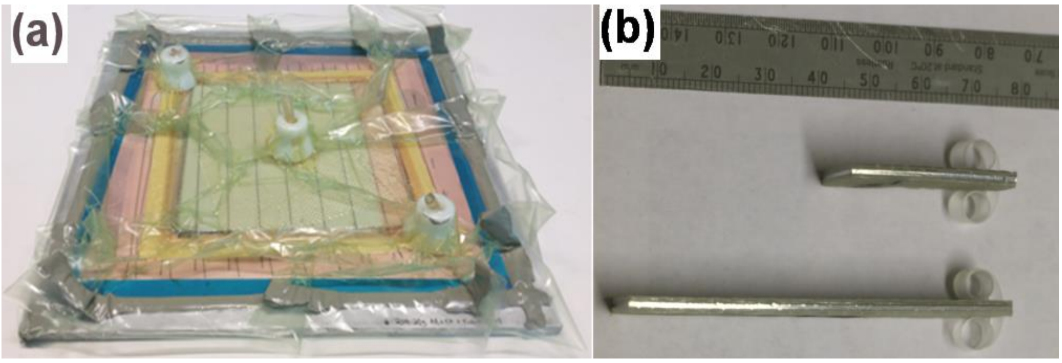

Fig 3: (a) VARTM process, (b) images of the extracted FML coupons

Table 2 Summary of preliminary mechanical test results.

	Lay-up	**Al thickness (mm)**	**Flexural Strength (MPa)**	**Flexural Modulus (GPa)**
FRP (Feasibility)	(4) UD¥ glass-fabric-Elium®	-	503±25	24.2±1.1
Alkali-FML (Feasibility)	(1/2) (Al/UD glass-fabric-Elium®)	0.71	462±45	27.9±1.4
Alkali- FML [5]	(3/2) (Al/glass-epoxy)	0.2	160±10	-

¥ Unidirectional (UD)

Table 3 Summary of ILSS results compared to the literature.

Material	Lay-up	Al thickness (mm)	Treatment	Shear strength (MPa)
FRP (Feasibility)	(4) UD¥ glass-fabric-Elium®	-	-	39.5±4.1
FML (Feasibility)	(1/2) (Al/UD glass-fabric-Elium®)	0.71	Alkali	20.2±5.3
FML-GLARE [6]	(4/3) (Al/glass-epoxy prepregs)	0.40	Alkali + PAA*	54±2
FML-GLARE [7]	(3/2) (Al/UD glass-epoxy prepregs)	0.30	Anodising	71±2
FML [8]	(2/1) (Al/long-fibre-Nylon66 composite)	-	Sandblasted	34.4

¥ Unidirectional (UD), * Phosphoric acid anodizing (PAA)

The ILSS values measured for the TPC-FML in the Feasibility Study were lower than the values found in published literature for thermoset FMLs and lower than the reference FRP laminate. Further optimisation of the bond strength is required to improve the ILSS property. The bond strength optimisation will be the key step in the core project. Along with epoxy acrylate, other organic adhesives/coatings will be used capable of participating in the in-situ polymerisation with the matrix resin. The amount and coating technique will be optimised.

- Metal-TPC interfaces of the manufactured FMLs were characterised using SEM which revealed fully-wetted FMLs with good interfacial bonding as seen in Fig 4(a–c). No void or gaps were evident at the TPC-metal interface.

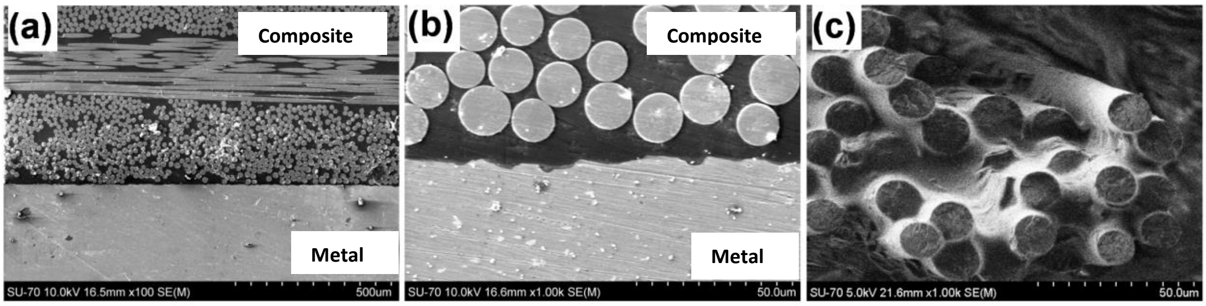

Fig 4: (a) SEMs of the FML cross sections (b) TPC-metal interface (c) fibre/ TP resin bonding at the interface.

- The metal-TPC bond strength was examined with a double cantilever beam (DCB) test and the obtained mode-I interlaminar fracture toughness G_{1C} results are displayed in the Table 4. FMLs with alkali treated metal interlayers were only subjected to the DCB tests. Other sets of FMLs were not ready for the test. It can be seen that G_{1C} values of the thermoplastic FMLs based on Elium® resin with alkali-treated metal interlayer revealed an enhanced mode-I interlaminar fracture toughness property compared to the thermoset FML based on epoxy resin with an alkali-treated metal interlayer [9]. Fig 5 (a) shows an image of the reference FRP specimen in the Mode I test. Fig. 5 (b) shows an image of the delaminating FML specimen (with alkali treated metal interlayer) during the DCB test, highlighting the fibre bridging in the wake of the delamination front. Fig. 6 depicts a typical delaminated FML sample after the DCB test. The delaminated metal part (Fig. 6c) clearly shows the impressions of the TPC layer indicating a reasonable level of bonding, which is also evident in the calculated G_{1C} values. The FMLs with the plasma treated metal interlayer became debonded during specimen extraction by CNC machining. The bonding between the metal and the TPC was weak in this case and further optimisation is required to enhance the bond strength. Manufacturing of new laminates could not be done due to time constraints and also non-availability of the plasma unit (the rented machine was returned).

Table 4 Average mode I interlaminar fracture toughness C_{IC} values according to ASTM 5528-01.

	Lay-up	Al thickness (mm)	G_{IC} (J/m^2)	Observations
Alkali-FML (Feasibility)	(1/2) (Al/UD glass-fabric-Elium®)	0.71	350±35	Average G_{IC} value of TPC-FML (Feasibility Study) was higher (+170%) compared to the reported thermoset-FML [7].
Alkali-FML [9]	(1/1) (Al/glass-epoxy)	1.5	131±3	
FRP (Feasibility)	(4) UD glass-fabric-Elium®	-	1251±105	

Average G_{IC} value of the TPC-FML (Feasibility Study) was higher (+170%) compared to the reported thermoset-FML case [7]. This is a promising observation. This value is likely to be enhanced further with further optimisation of the bond strength.

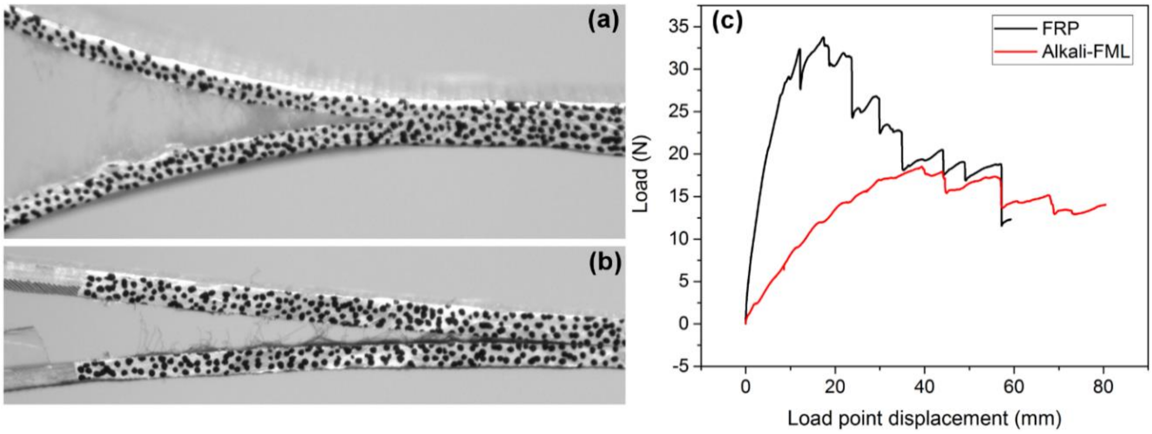

Fig 5. Typical (high) speed images of the crack tip zone in detail of (a) FRP and (b) FML (alkali treated metal interlayer) and (c) load/extension curves of the two cases during Mode I fracture toughness test.

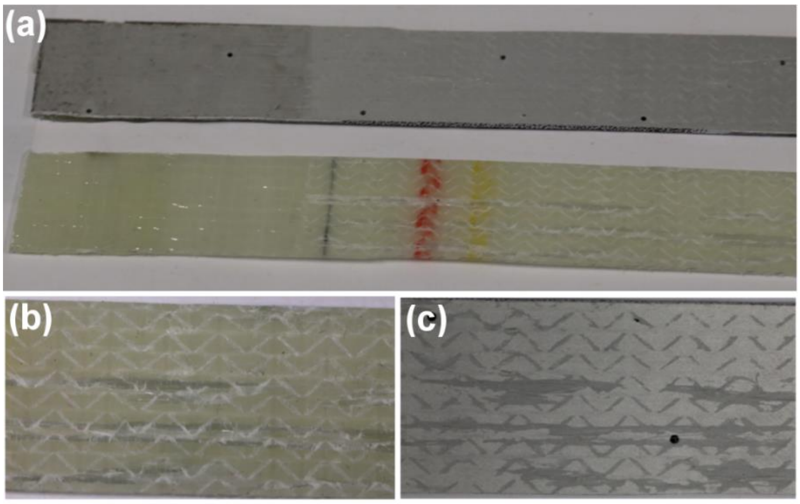

Fig 6. Typical images of delaminated FML (with alkali treated metal interlayer) after DCB test (a) metal and TPC separated after DCB test (b) delaminated TPC part (c) delaminated metal part with impressions of TPC on it.

- Drop weight impact tests of TPC-FMLs with alkali treated metal interlayers were performed in comparison with baseline FRP laminates in accordance with ASTM D7136. Samples were subjected to 15 J (equivalent velocity: ~2 m/s) impacts on a Rosand Type 5 H. V. falling weight impact tester (University of Nottingham) with a falling weight of 8.87 kg and height of 0.24 m; a 12.5 mm diameter hemispherical impact striker was used. Typical force-displacement curves are displayed in Fig 6.

  Reference laminates were found to exhibit consistent impact face and back face damage modes; the primary impact face mode being indentation and minimal fibre splitting along the 0° ply (Fig 7a), while a combination of fibre splitting and delamination was observed on the back face (Fig 7b). FMLs (alkali treated metal interlayer) were observed to exhibit a lesser extent of fibre splitting on the impact face (Fig 7c); however, slight indentation occurred in all cases. Some extent of localised plastic deformation was observed upon visual inspection of the back face damage, possibly as a result of the deformation of the metal layer (Fig 7d). The FMLs were found to exhibit some plastic deformation resulting in disbonding at the fibre-metal interface on the impact side and a circular shaped disbond area which coincided with the site of back face delamination (Fig 7d – e). Mean absorbed energies were evaluated as 14 J ± 1.67 and 14.6 J ± 1.3 for the reference and FML, respectively. These corresponded to mean peak loads of 6.1 kN ± 1.6 and 5.7 kN± 1.8, respectively.

Although other authors have primarily focused on FMLs with externally-placed metallic sheets, for comparison purposes, reported damage modes in published literature were compared with the findings of this study. All authors [10-11] reported that localised plastic deformation of the Al sheets predominated in terms of energy absorption for low-energy impact tests (10 J to 25 J range). In one case, indentation and plastic deformation were the only modes described [10], however, contact zone cracks were observed in impact and back face Al sheets in other studies [11-12]. Peak loads reported for a 20 J impact events ~5 kN [11] and ~8 kN [12].

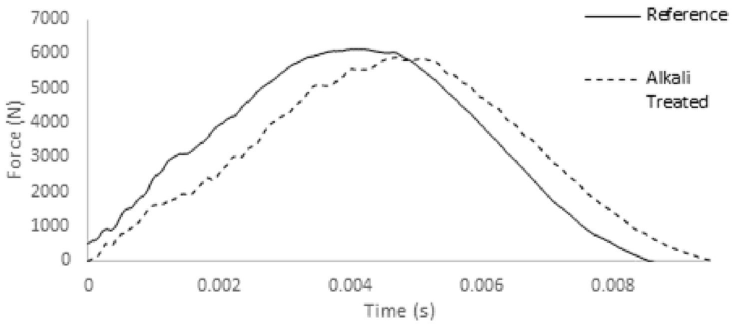

Fig 6: Representative force-displacement curves of the two cases examined i.e. FRP and TPC-FML with alkali treated metal interlayer.

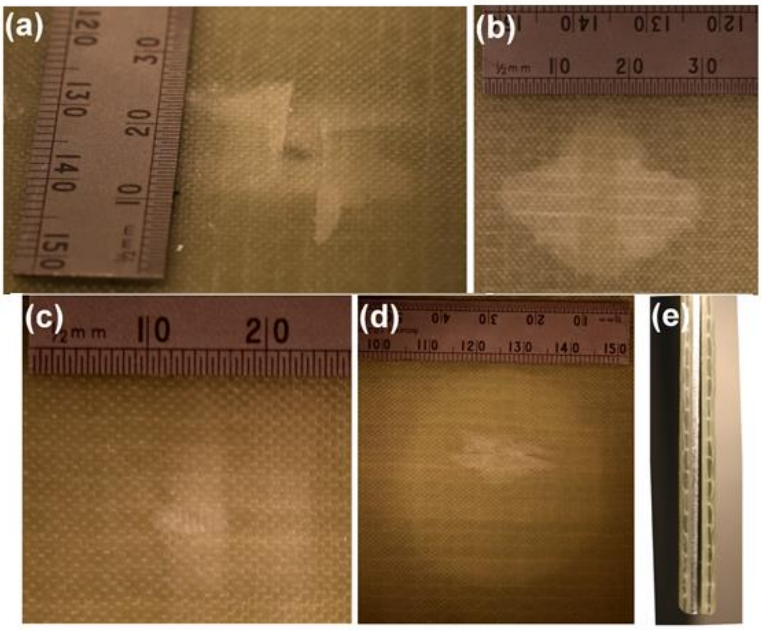

Fig 7. Typical images of the impact tested specimens with (a) impact face FRP, (b) back face FRP, (c) impact face of FML with alkali treated interlayer, (d) back face of FML with alkali treated metal interlayer and (e) disbonding at the fibre-metal interface.

Residual Stress generation during manufacturing is a serious problem in FMLs as the coefficient of thermal expansion values are significantly different for the metal and the composite. The manufacturing of the TPC-FML was done by resin infusion technique at room temperature in this study. The exotherm generated was monitored for the reference FRP laminate as well as for the TPC-FML by recording the rise in temperature during the in-situ polymerisation process, as shown in Figure 8. Two thermocouples (K-type) were placed at the edges of the intermediate ply of each lay-up prior to VARTM process and the temperature was recorded during the whole process. It is evident that the presence of the metal interlayer in the FML resulted in a higher rise in temperature compared to the FRP, owing to the different physical properties i.e. thermal conductivity and heat capacity. The temperature rise was nominal and not likely to generate residual stress in the material. This will be further investigated in the core proposal.

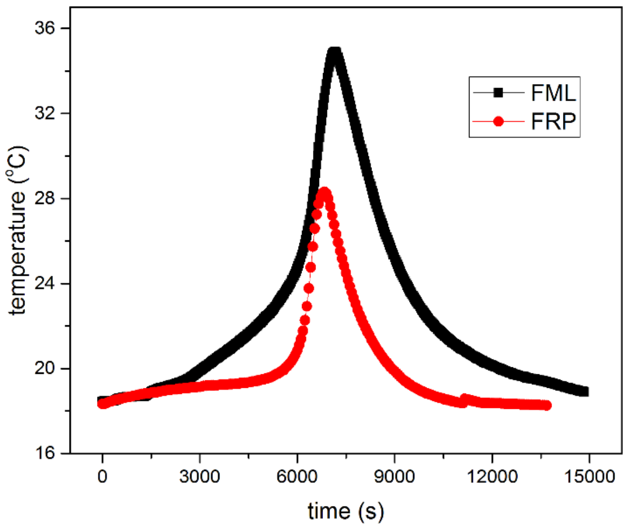

Fig. 8: Temperature profile in the FRP and the TPC-FML during in situ polymerisation and composite manufacturing process.

Key Findings

- Suitable surface treatment conditions were identified for the Al alloy sheets (10% NaOH treatment for 20 min, atmospheric plasma treatment with 2 mm/s scan speed, 1 scan and source(nozzle)-to-substrate distance 0.5 mm). Anodisation was done from an external agency.
- VARTM manufacturing of the TPC-FMLs was successfully carried out using Elium® liquid thermoplastic resin.
- Test samples were successfully extracted from the TPC-FMLs for mechanical testing without any debonding at the TPC-metal interface (except two laminates from last batch).
- Reference FRP and TPC-FMLs were characterised for their flexural and interlaminar shear strength properties. The measured properties were in comparable range with the published literatures.
- TPC-metal bond strength was measured with DCB test. Mode-I Interlaminar fracture toughness of the thermoplastic FML (Elium® resin/glass fibre and alkali treated metal interlayer) was found to be (~170%) higher than the reported value of epoxy based thermoset FML [8].

A novel way of bonding Al alloy sheets (with an organic coating) and thermoplastic composite layers through the in-situ polymerisation technique was found to be successful.

Challenges

- Two laminates from the last batch were delaminated during sample extraction by CNC, Bond strength optimisation is crucial. Cutting and machining of FMLs need good understanding and optimisation.
- The lay up sequence of TPC and metal layers needs optimisation through modelling to achieve the highest combination of properties.

Future Direction

- Achieving optimised metal-TPC bond strength by a suitable technique which is industrially viable.
- Optimisation of the FML manufacturing process with greater understanding and minimum processing defects.
- Generating mechanical property data with thorough investigation of the damage and failure processes.
- Investigating fatigue and creep behaviour of the FMLs.
- Preliminary investigations of the recyclability, weldability and repairability of the FMLs.
- Commercial evaluation of the technology.

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