CLOSED-LOOP RECYCLABLE AND FIRE-RESISTANT COMPOSITES FOR ELECTRICAL CAR BATTERY BOXES

P. Ares-Elejoste [1], J. Ballestero [1], G. Creonti [2], S. Bassi [3], C. Valli [3] and C. Mingazzini [4]*

[1] *GAIKER Technology Centre, Parque Tecnológico de Bizkaia, Edificio 202, 48170 Zamudio, Spain;*
[2] *Crossfire srl, Via Volta A., 22, 48022 Lugo RA, Italy;*
[3] *Certimac soc. cons. a r.l., Via Granarolo 62, 48018, Faenza, RA, Italy;*
[4] *ENEA SSPT-TIMAS-MCC, via Ravegnana 186, 48018, Faenza, Italy*
* *Correspondence*: claudio.mingazzini@enea.it

ABSTRACT: Increasing battery energy density (Wh/kg) in electric cars implies higher fire risk and requires that the corresponding battery boxes act as a barrier to fire and overheating, whether they originate from the battery itself or from external sources. Weight and volume reduction, as well as recyclability, are equally important in the automotive sector due to stringent EU regulations on carbon footprint, both during use and at end-of-life. Although steel and aluminium have traditionally been considered acceptable options, long fiber-reinforced composites offer greater potential for weight reduction and fire resistance, provided they are properly engineered and qualified. This paper discusses Fiber Metal Laminates (FMLs) as a promising solution. To ensure sustainability, the use of biobased, secondary, and closed-loop recyclable raw materials was studied. Regarding the resins, both biobased polyfurfuryl alcohol resin and a closed-loop recyclable epoxy-polyester hybrid resin outperformed standard epoxy resins in terms of both fire resistance and sustainability. They also enabled higher post-fire performance, as demonstrated in a 10-minute ISO 5660-1 cone calorimeter test at 50-60 kW/m^2, simulating surface temperatures between 600 and 700 °C. All the developed FML materials also passed powder erosion tests at 600 °C, as required for Lithium Iron Phosphate batteries. Basalt and glass fibers, used as reinforcement, allow for closed-loop recycling.

Keywords: closed-loop recyclability, fire-resistance, battery-boxes, FML, fiber metal laminates, cone calorimetry

1. INTRODUCTION

Fiber Metal Laminates (FML) allow weight reduction of battery boxes, along with fire resistance, although up to now production costs and closed-loop recyclability are still unsolved issues [Costa, R. D. F. S. (2023)]. These were the main objectives of FENICE (upscaling, KAVA9, EIT RawMaterials, www.fenice-composites.eu, 2022-2025) an EU project, funded with over 2.5 million and aiming at TRL 7, focusing on fire resistant battery boxes, for increasing safe use of current lithium-based battery modules. The application demands structural optimisation in terms of weight reduction and vibration management, which are the main requirements in the automotive field. The first resonance frequency of each component depends essentially on weight and rigidity (elastic modulus). To meet automotive OEM requirements in terms of resonance frequencies, a solution must be identified that provides adequate rigidity while still ensuring significant weight reduction. To avoid resonance effects with the vibrations caused by the engine and road, resulting in unacceptable noise, a general criterion is ensuring that the first resonance frequency is beyond 30 Hz. Fiber Metal Laminates (FML) with monolith and sandwich structures including different composite layers, reinforced with glass, basalt and carbon plain balanced fabrics are being compared in terms of mechanical properties. Biaxial and quadriaxial non-woven fabrics were also considered, allowing increased fiber-to-matrix (F/M) ratios. The F/M in all considered composite layers was kept in the range 65/70%v/v. The study carried out aimed to evaluate and validate the introduction of a core structure in the lamination of FML composite materials. Elium resin (and the related composites) has been patented in several patents [Bachman, N.J. (2024), Bozsak, V. (2024)], and the same is being done with Crossfire one, including an application about FML component production [Creonti, G. (2024), Mingazzini, C. and Creonti G. (2025)]. FMLs based on Elium and Crossfire resins are both thermomouldable after curing at 200℃, so they can be remolded at high temperature, for example for past production of square-waved cell spacers and battery boxes [Mingazzini, C. (2022)].

2. MATERIALS AND METHODS

Monolithic and sandwich composite panels were produced using prepregs based on either Crossfire resin (www.crossfire-srl.com/en/) or polyfurfuryl alcohol (PFA, www.transfurans.be) [Elejoste, P. A. (2022)], with carbon, basalt, or glass fabrics. Composites were produced at 160-180°C and combined with 10 mm thick cores in recycled PET (RPET) by Armacell® (150 kg/m^3, GRX150®), supporting processing in a warm press. All mechanical tests, before and after cone, were performed applying relevant international standards (e.g. ASTM D-790). 1x1 m^2 panels were produced, using different types of prepreg (Crossfire resin-glass, PFA-carbon, Elium-basalt). For comparison, also an aeronautical grade epoxy glass-based prepreg (with and without a surface aluminium layer on top) and Elium resin (Arkema, www.arkema.com) [Bachman, N.J. (2024), Bozsak, V. (2024)] and infusion processing were considered. The effect of aluminum thickness (0.02-0.5 mm) was investigated, considering both its use as a top surface layer and its integration within the laminate structure. For the comparative study, the following composite panels were prepared by warm pressing (Table 1a, monolithic FMLs and composites, Table 1b, FML sandwiches and Table 2, monolithic FMLs at increasing thickness). Steel was considered as a possible alternative to aluminium as top layer, but then abandoned, since aluminium (even when used at very thin thickness) allowed to achieve the expected performances, and is lighter and cheaper.

Table 1a. Different laminations and curing conditions for the monolithic FMLs and composite samples

Sampling ID	Sample lamination	Curing T
CROSS-M1	Al 0.1 mm | CrossPreg (based on glass fabrics), 6 plies | Al 0.1 mm	180°C 5 min, 6 bar
CROSS-M2	Steel 0.1 mm | CrossPreg (based on glass fabrics), 6 plies | Steel 0.1 mm	180°C 5 min, 6 bar
PFA-M1	Al 0.02 mm | PFA (based on C fabrics, 400 gsm), 4 plies | Al 0.02 mm	180°C 10 min, 6 bar
ELIUM-1	Al 0.5 mm | Elium basalt Multiax, 600 gsm, 3 plies +/- 45°| Al 0.5 mm	RT 24 h, 1 bar
ELIUM-2	Al 0.5 mm | Elium basalt Multiax, 600 gsm, 8 plies +/- 45°| Al 0.5 mm	RT 24 h, 1 bar
EPOXY-1	Aeronautical-grade Epoxy Glass, 400 gsm fabrics, 12 plies	130°C 30 min, 6 bar

EPOXY-2	Al 0.02 mm | Aeronautical-grade Epoxy Glass, 400 gsm, 12 plies | Al 0.02 mm	130°C 30 min, 6 bar

Table 1b. Different laminations and curing conditions for the sandwich FMLs samples

Sampling ID	Sample lamination	Curing T
CROSS-S1	Al 0.1 mm | CrossPreg glass, 600 gsm, 1 ply | RPET, 150 gm^2, 10 mm | CrossPreg glass, 600 gsm,1 ply | Al 0.1 mm	180°C 5 min, 6 bar
CROSS-S2	Al 0.1 mm | CrossPreg glass, 600 gsm, 2 plies | RPET, 150 gm^2, 10 mm | CrossPreg glass, 600 gsm, 2 plies | Al 0.1 mm	180°C 5 min, 6 bar
CROSS-S3	Al 0.1 mm | CrossPreg glass, 600 gsm, 3 plies | RPET, 150 gm^2, 10 mm | CrossPreg glass, 600 gsm, 3 ply | Al 0.1 mm	180°C 5 min, 6 bar
PFA-S1	Al 0.1 mm | PFA Basalt fabrics, 650gsm, 2 plies | RPET, 150 gm^2, 10 mm | PFA Basalt, 650gsm, 2 plies | Al 0.1 mm	180°C 10 min, 6 bar

Table 2. Different laminations and curing conditions for the FML samples, produced to inquire thickness effect

Sampling ID	Sample lamination	Curing T
CROSS-M4	Al 0.1 mm | CrossPreg, quadriax glass, 800gsm, 4 plies | Al 0.1 mm	180°C 5 min, 6 bar
CROSS-M5	Al 0.1 mm | CrossPreg, quadriax glass, 800gsm, 5 plies | Al 0.1 mm	180°C 5 min, 6 bar
CROSS-M6	Al 0.1 mm | CrossPreg quadriax glass, 800gsm, 6 plies | Al 0.1 mm	180°C 5 min, 6 bar

A cone calorimeter (ISO 5660-1:2015 + Amd 1:2019) was used. Specimens (100 × 100 mm) were irradiated, and the heat release rate (HRR) was calculated based on oxygen consumption. THR (Total Heat Released, MJ/m^2), MARHE (Maximum value of the Average Rate of Heat Emission, kW/m^2), ignition, extinction and Qmax time for monolithic and sandwich FML and composite samples were recorded to classify the materials according to relevant international standards EN 45545 (railway sector), EN ISO 1182: 2020 (“Reaction to fire tests for products”) and EN 13501-1 (“Fire classification of construction products and building elements. Part 1: Classification using data from reaction to fire tests”) and EN ISO 13823 (“Single Burning Item”, SBI, test). The adopted cone calorimeter test conditions were:

- Distance between the specimen surface and the cone: 25 mm
- Radiation on the exposed face: 50 and 60 kW/m^2 (producing an approximate surface temperature around 600 and 700°C)
- Exposure times: 10 min and 20 min
- Spark placed above the specimen, switched off, as soon as the specimen ignites

Another very important test, for simulating thermal runaway of lithium batteries, is the high temperature powder erosion test, which simulates the abrasion caused by the debris produced during the process. For simulating such conditions, most automotive OEMs adopt a test that uses a setup such as the one in Figure 1. In the present study, aiming at validating battery boxes for lithium iron phosphate, the tests were performed at 600°C for 60 seconds while powder jetting, using alumina, at a rate of 5 g/s, after a preheating at 600℃ for another 60 seconds without particles. The samples were heated using a radiative source, quite like the system used for the cone calorimeter, at 25 mm distance and with a heat flux of 50 kW/m^2. Regarding the alumina ceramic powder, high purity aluminum oxide was used, with a mesh size in the range of 60 - 150 µm, with 50% of particles having an average diameter greater than 100 µm. The composite samples were subjected to the action of the radiation combined with the erosion due to the particles, while a camera recorded the whole test for the set time and post-test weight and geometry measures. Analysis was repeated on the same type of samples more times to have different measurements and to extract a mean value representative of the sample.

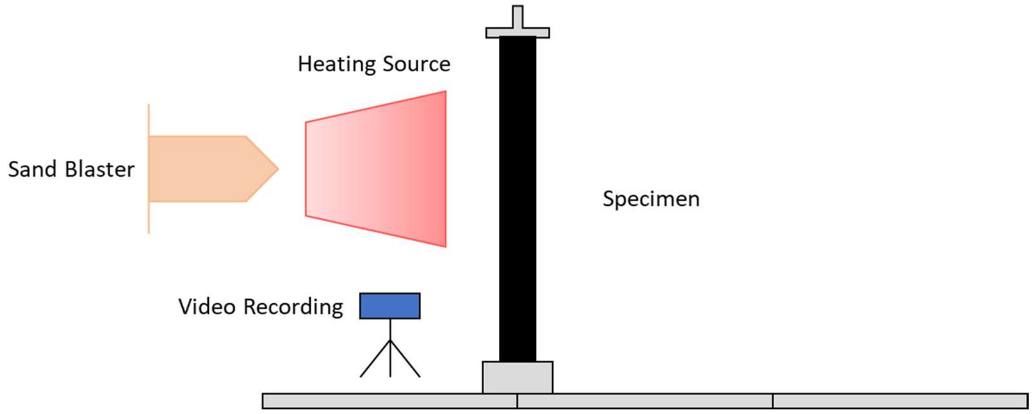

Figure 1. Protocol for high T powder erosion test, for lithium iron phosphate batteries: setup diagram.

3. RESULTS AND DISCUSSION

The samples, both monolithic and sandwich, have been tested at the cone calorimeter for about ten minutes, at 60 kW/m^2. The results in table 3 have been achieved, through multiple runs on samples made of the same material, by averaging the experimental values on the different samples.

Table 3. MARHE, THR, ignition, extinction and Q_{max} time for monolithic and sandwich FML and composite samples

Samples @ 60 kW/m²	**MARHE (kW/m²)**	**Ignition time (s)**	**Q_{max} time (s)**	**Extinction time (s)**	**THR (MJ/m²)**
		MONOLITHIC SAMPLES			
CROSS-M1	29 ± 3	-	3	-	-
CROSS-M2	31 ± 6	-	1	-	0.4
PFA-M1	7 ± 3	-	4	-	1.9
ELIUM-1	141 ± 4	57	77	131	18.5
ELIUM-2	135 ± 4	39	216	453	46.4
EPOXY-1	66 ± 4	225	147	599	24.8
EPOXY-2	7 ± 2	585	537	> 730	6.7
		SANDWICH SAMPLES			
CROSS-S1	20 ± 13	529	596	> 600	6.8
CROSS-S2	14 ± 12	-	2	-	0.5

CROSS-S3	5 ± 1	-	2	-	0.1
PFA-S1	19 ± 2	507	476	> 600	10.2

These data have made it possible to identify some key points necessary for identifying the best structure to ensure the best performance, both mechanical and in terms of fire resistance. Firstly, analyzing the two monolithic samples made with epoxy resin, the importance of using aluminium in the structure is clear: the EPOXY-M2 sample differs from EPOXY-M1 precisely because of the presence of a thin layer of Al 0.02 on the surface. This addition significantly reduces the MARHE while increasing the time at which maximum surface heat is recorded, thus significantly increasing the fire resistance of the sample. Having established this, attention is then shifted to the type of resin used, comparing the various monolithic samples analyzed. PFA showed acceptable fire-resistance properties in both monolithic and sandwich samples, and satisfactory adhesion on special pretreated (sized) aluminium but water evolution during curing makes it difficult to produce FMLs fast and reliably. Therefore, the main comparison with epoxy resin was made using Crossfire and Elium-based samples, in both the monolithic sample and the sandwich sample. The use of ELIUM resin, as shown by the results above, leads to a deterioration in fire resistance: this is probably because the infusion process requires the aluminium layer to be perforated, which therefore no longer acts as an effective oxygen barrier. Among the resins tested, Crossfire resin provided the most suitable alternative to epoxy. It not only maintained satisfactory fire resistance but also offered two significant advantages: on the one hand, the transition from a monolithic structure to a sandwich structure through the introduction of a recycled PET core is not only possible but also maintains acceptable fire resistance properties. On the other hand, Crossfire's patented resin is a chemically recyclable epoxy-polyester hybrid, which makes it possible to recycle production scraps and the components at the end of their life, something that epoxy resin does not allow: what is recovered is BHET and epoxy oligomers, which can be used to produce the starting Crossfire resin again, with no performance degradation. In addition to those significant points, Crossfire resin outperforms epoxy even in post-fire performance: after a 10-minute cone calorimeter test, the flexural strength of epoxy composites is no longer measurable, while Crossfire composites retain significant strength, as shown in Table 4.

Table 4. MARHE, strength and modulus, and residual values (R%) after 10 min fire exposure, for monolithic samples

Samples	**MARHE (kW/m^2)**	**Flexural Strength (MPa)**	**Flexural Modulus (GPa)**	**Residual (R%)**	
				Strength	**Modulus**
Heat flux = 50 kW/m^2, T ~ 600°C (10 min)					
CROSS-M4	2,64	613 ± 40	15.7 ± 0.4	~ 66%	~ 63%
CROSS-M5	3,96	585 ± 17	15.7 ± 0.9	~ 82%	~ 84%
CROSS-M6	3,15	613 ± 41	18.7 ± 1.9	~ 65%	~ 58%
Heat flux = 60 kW/m^2, T ~ 700°C (10 min)					
CROSS-M4	3,20	613 ± 40	15.7 ± 0.4	~ 22%	~ 36%
CROSS-M5	1,98	585 ± 17	15.7 ± 0.9	~ 64%	~ 59%

CROSS-M6	2,39	613 ± 41	18.7 ± 1.9	~ 69%	~ 76%

The samples M4, M5, and M6 were produced to investigate the effect of thickness in monolithic samples, showing that a higher number of plies enhances post-fire flexural strength (10 min at 50 or 60 kW/m^2). The table also reports residual strength percentages (R%), which increase with thickness, as the glass-based composites are highly thermally insulating and help preserve the mechanical integrity of inner layers not exposed to peak temperatures. Residual strength after fire reached 60-80% for M5 and M6, despite only a 0.02 mm Al top layer. This was an unexpected outcome and represents one of the most significant results of the Fenice project (co-funded by EITRM, www.fenice-project.eu). Some of the samples were also subjected to the powder erosion test, performed in accordance with typical automotive OEMs testing procedures, described in the experimental part. The results are shown in Table 5.

Table 5. Powder erosion test results (at T~ 600 °C, 120 sec)

Samples	Weight Variation (%)	Thickness Variation (%)
CROSS-M1	0.0 %	-3.3 %
CROSS-M2	-0.1 %	+6.5 %
CROSS-S3	0.0 %	-9.2 %

All samples subjected to the powder erosion test passed the test, with virtually no weight loss or thickness variations caused either by bending of the samples themselves or by the formation of small bulges, due to deformation of the sample itself. In all cases, FML passed the tests, meaning that no hole was formed and very limited delamination between aluminium and composite layer (see figure 2).

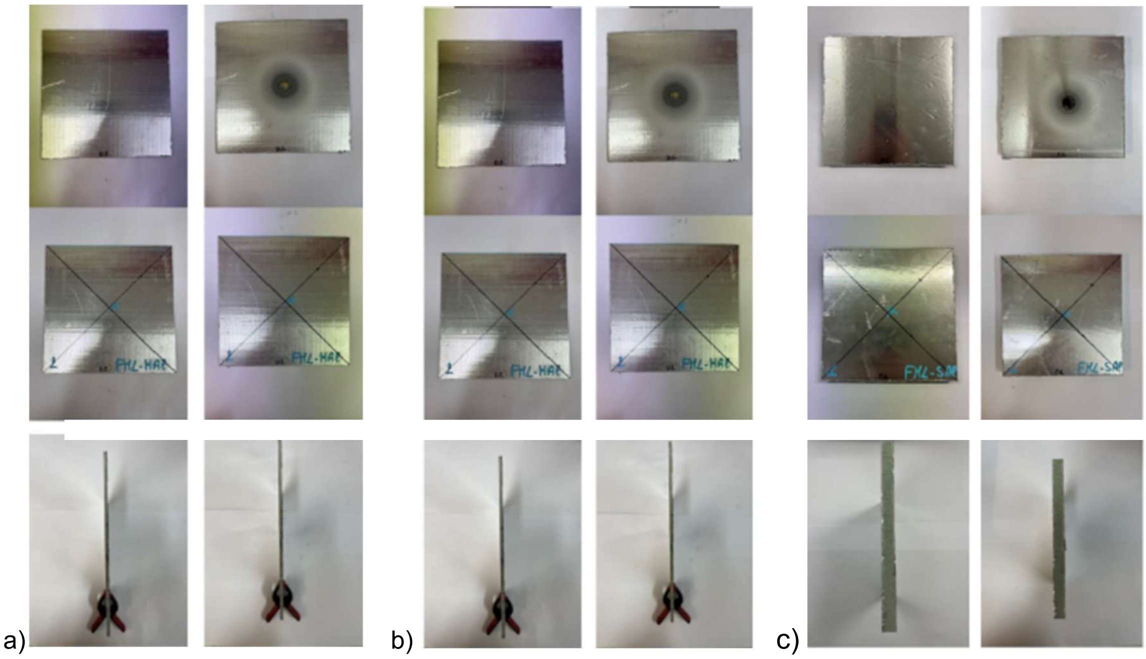

Figure 2. From left to right, CROSS-M1 (a), CROSS-M2 (b) and CROSS-S3 (c) before (figures on the left) and after (figures on the right) the high temperature powder erosion test

Considering the encouraging results on Crossfire based-FMLs, flexural tests were also performed on

CROSS-M1, after 20 minutes cone calorimeter exposure at 700 °C, finding an encouraging residual flexural strength around 55% and residual flexural modulus of 58%. These data suggests that glass fabric reinforcement outperforms multiaxial basalt in post fire mechanical properties, which is reasonable.

4. CONCLUSIONS

The tests carried out on the composite samples made it possible to exclude epoxy resins for battery boxes application, since, even in the FML structure, they do not retain residual mechanical properties after fire. This showed the need to develop FMLs with innovative and more sustainable resins. Biobased PFA resin showed good results also in terms of adhesion to aluminium, provided that properly pretreated (sized) aluminium was used, but water evolution during curing makes it difficult to produce large and complex components in warm pressing, when a top aluminium layer is needed. Without aluminium top layer, PFA resists to fire in terms of weight loss and MARHE, but residual flexural strength after fire is not measurable. On the other hand, the closed loop recyclable resin patented by Crossfire, an hybrid of epoxy and polyester resins, allows significant mechanical properties after exposure to 700 °C for 10 min (residual flexural strength and modulus up to 70%) and even 20 minutes (residual flexural strength and modulus up to 50-60%). The aluminium, working as a heat mirror and oxygen barrier, can be very thin (0.02 mm) and does not interfere with large components production, since the resin is VOC- and solvent-free. The sandwich structure can include a RPET core which does not interfere with end-of-life recycling (both the resin and the core are chemically recycled to recover BHET, which can be closed loop reused for new battery boxes, with no downgrading) and does not reduce fire resistance too much. A sandwich structure is being considered for increasing rigidity [Mingazzini, C. 2025], which is necessary to comply with first resonance automotive requirements, aimed at limiting noise transmission from road and engine.

ACKNOWLEDGEMENTS

The article was written based on the results of tests carried out as part of the Fenice Project (Upscaling n° 21099, 2022-25, www.fenice-composites.com), co-funded by EIT Raw Materials.

REFERENCES

Bachman, N.J., Barsotti, R.J. (2024). *Weldable thermoplastic composite composites* (Patent No. US12134234B2) United States Patent. https://patentimages.storage.googleapis.com/50/b7/92/ed46f711cf1570/US12134234.pdf.

Bozsak, V., Cledat, G., Gerard, P., Glotin, M. (2024). *Process for manufacturing thermoplastic polymer composite parts, and object obtained by said process* (Patent No. EP3595873A1). European Patent Office

Costa, R. D. F. S., Sales-Contini, R. C. M., Silva, F. J. G., Sebbe, N., & Jesus, A. M. P. (2023). A critical review on FMLs: From manufacturing to sustainable processing. *Metals*, *13*(4), 338. https://doi.org/10.3390/met13040638

Creonti, G. (2024) *Composizione reticolabile ibrida epossidica-poliestere, composizione reticolata ibrida epossidica-poliestere, e relativo metodo di produzione, uso di almeno un reagente monometrico e/o oligomerico* (Patent Application No. 102024000013807)

Elejoste, P. A., Allue, A., Ballestero, J., Neira, S., Gómez-Alonso, J. L., & Gondra, K. (2022). Development and Characterisation of Sustainable Prepregs with Improved Fire Behaviour Based on Furan Resin and Basalt Fibre Reinforcement. *Polymers*, 14(9), 1864. https://doi.org/10.3390/polym14091864

Mingazzini, C., Pullini, D. Basso, M. (2022) *Battery pack, and assembling process for manufacturing a battery pack* (EP4463911 A1, WO2023/135546)

Mingazzini, C., Creonti, G. (2025) *Metodo per la realizzazione di un componente in materiale composito di elevate dimensioni* (Patent Application No. 102025000009861)

Mingazzini, C., Scafè, M., Mariani, E., De Aloysio, G., Morganti, M., Laghi, L., Ghetti, L., Bassi, S., & Valli, C. (2025). Fiber Metal Laminates for battery boxes: a compromise between strength and rigidity [Paper in congress proceedings]. After oral presentation at ICEAF VIII, Kalamata (Greece), June 22-25, 2025, https://iceaf.eu/