

Blast and Fire Resistant Material

BAM

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DESIGN AND DEVELOPMENT OF

HYBRID LAMINATED MATERIAL (HLM)









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EXECUTIVE SUMMARY

The key objective of the research project "*Blast and Fire Resistant Materials (BAM)*" was the design and development of innovative, sustainable, and low cost construction materials, with combined blast/impact- and fire-resistance. These materials were aimed to be capable of dispersing the energy of blast/impact loads by enhancing their ductility and toughness and simultaneously, protecting the structure from a fire incident that may follow or proceed. Specifically, BAM research project deals with the design and development of (i) a Hybrid Laminated Material (HLM) in WP3, Task 3.1, which consists of an Ultra-High Performance Fibre Reinforced Concrete (UHPFRC) with blast and impact resistance and a superficial layer of a fire resistant geopolymer (FRG) and (ii) a Smart Composite Geopolymer Concrete (SCGC) in WP3, Task 3.2, which has dual functionality, i.e., of fire and blast/impact resistance.

Deliverable "*D3.1- Design and Development of Hybrid Laminated Material (HLM)*" presents the work performed to design and develop a two-layered Hybrid Laminated Material with blast, impact and fire resistance to be used for protecting new and existing buildings and constructions (Task 3.1). Moreover, Deliverable D3.1 includes the results of the study performed to assess the interlayered adhesion bond of the two materials (UHPFRC and FRG) in the HLM.

The consortium has successfully designed and developed an UHPC material reinforced by steel and PVA fibers (UHPFRC) that exhibited compressive strength higher than 150 MPa and flexural strength of 22.6 MPa, which indicates very high potential for blast and impact resistance. This property of the developed UHPFRC was confirmed in WP4, Task 4.3 and the results are presented in the Deliverable "*D4.2-Validation of Materials in the Laboratory*". In addition, the consortium has successfully designed and developed fire-resistant geopolymers based on fly ash, which presented thermal stability and good mechanical performance after their exposure to high temperatures, up to 1050 °C. The fire resistance of the optimum materials was evaluated according to the standard ISO 834 time-temperature curve (WP4, Task 4.3) and the results are included in the Deliverable "*D4.2-Validation of Materials in the Laboratory*". The casting process flowsheets followed to produce both the UHPFRC and FRG materials that are used as layers in the HLM are also developed and presented in the Deliverable "*D4.1-Flowsheet of Materials Production*".







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1. Introduction

A key task planned and implemented in the frame of in the research project "*Blast and Fire Resistant Materials (BAM)*" was the design and development of a Hybrid Laminated Material that comprises a blast- and impact-resistant layer of Ultra High Performance Fibre Reinforced Concrete (UHPFRC) and a fire-resistant layer of a geopolymer material based on industrial wastes and byproducts. Specifically, in WP3, Task 3.1 of the project, the development of HLM was scheduled through a series of experiments, to define the composition and properties of the layered materials that constitute the composite HLM. This experimental study resulted in the optimization of mix designs for the casting of both layered materials and the process flowsheet that fulfil the operational requirements for the layered materials production (details are given in the deliverable "*D4.1 - Flowsheet of Materials Production*"). Based on the optimized UHPFRC and FRG materials and the processing flowsheets, the production of HLM was achieved and the adhesion bond of the two layers was assessed. The present deliverable "*D3.1-Design and Development of Hybrid Laminated Material (HLM)*" includes the results of this effort.







2. Design and Development of the UHPFRC Layer

The Ultra High-Performance Fibre Reinforced Concrete (UHPFRC) material, which was targeted to be used as the blast- and impact-resistant layer of the new Hybrid Laminated Material (HLM) developed in the BAM project, was designed and developed by the partner UCY (University of Cyprus) in close collaboration with FRC (Frederick Research Center). The design and development of this material was based on a reference UHPFRC (Ultra High Performance Fiber Reinforced Concrete) mixture studied in the paper titled "Mix design and mechanical properties of ultra-high-performance fiber reinforced cementitious composites (UHPFRCCs)", by Nicolaides D., Kanellopoulos A., Savva P., Mina A., Petrou M. (2013) at the "Proceedings of the 1st International RILEM Conference on Rheology and Processing of Construction Materials", (Paris, France). The UHPFRC reference mixture contents are demonstrated in Table 1.

Table 1: Reference mixture of UHPFRC.			
Constituent	Content (kg/m ³)		
Cement	880		
Microsilica	220		
Sand 125-250µm	475		
Sand 250-500µm	358		
Water	172		
Superplasticizer	67		
Steel fibers 6mm	401		
Steel fibers 13mm	80		
Water/Binder	0.16		

The mentioned mixture required an optimum microsilica content of 20%, a water/binder ratio of 0.16, heat curing for 7 days at 90 °C and a steel fiber content of 6% with 3:1 fiber ratio (short to long), achieving compressive and flexural strengths exceeding 150 MPa and 20 MPa, respectively. However, the reference mixture relied on locally sourced sand that needed to be sieved into two different grades (125-250 µm and 250-500 µm). This process was costly and most importantly time-consuming and thus caused significant delays. Therefore, the possibility of substituting the local sand with standard silica sand was explored. In addition, as observed in Figure 1, further reduction in the steel fibre content was successfully employed, without sacrificing achievement of the project's required strength goals. Consequently, two mixtures were investigated: one with a steel fibre content of 2% and a 1:1 short to long ratio, and another with 2% steel fibres, along with 1% polyvinyl alcohol (PVA) fibres. These mixtures were examined for their compressive strength (EN 12390-3) on the 14th and 28th day, as well as their flexural strength (EN 12390-5) on the 28th







day. As depicted in Figure 2, modifying the steel fiber ratio from 3:1 to 1:1 enhanced the 28-day compressive strength, although it did not reach the target of 150 MPa. However, formulations containing 2% steel fibers (1:1 short to long ratio) and 1% PVA, along with the replacement of local sand with standard silica sand, met the project's minimum compressive strength requirement of 150 MPa.



Figure 1. 28-day compressive and flexural strength at varied steel fiber contents (3:1 short to long).



Figure 2. (a) Compressive of mixture containing 2% steel fibers (1:1) and 2% steel fibers (3:1); (b) mixtures containing 2% steel fibers (1:1) and 1% PVA.

Further optimization and examination of the flexural strength properties were conducted for various formulations containing steel and PVA fibres, with a step increment of 0.5% in each mixture. As anticipated and observed in Figure 3, increasing the fibre content resulted in higher flexural strength, with mixtures containing minimal fibre amounts exhibiting the lowest values.

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The mixture containing 2% steel fibres (1:1 ratio) and 1% PVA fibres demonstrated the highest flexural strength value of 22.64 MPa, surpassing the required target of 20 MPa.



Figure 3. Combinations of PVA and steel fiber contents and their effect on flexural strength.

The optimization process focused on developing the most environmentally friendly version of a UHPFRC mixture that meets the required compressive and flexural strength. The optimum UHPFRC mix design selected for the BAM Hybrid Laminated Material (HLM) and its determined mechanical properties are summarized in Table 2.

Constituent	Content (kg/m ³)	Material Property	Value	Unit
Cement	880	Density	2270	Kg/ m ³
Microsilica	220	Compressive Strength (100x100x100 mm Cubes)		MPa
Reference Sand	833	Modulus of Elasticity (Cylinders in Compression)	55.72	GPa
Water	172	Poisson's ratio	0.24	-
Superplasticizer	67	Tensile strength (50x25mm dog-bone)	10.53	MPa
Steel fibers 6mm	80	Modulus of Elasticity (direct tension on dog-bone)	50.56	GPa
Steel fibers 13mm	80	Tensile strength (prisms of cross sectional area 100x50mm)	8.9	MPa
PVA fibers	13	Modulus of Elasticity (direct tension on prisms)	39.5	GPa
Water/Binder ratio	<i>w/b</i> = 0.16	Flexural Strength (100x100x500 mm prismatic beams – 3 point bending)	29.47	MPa

Table 2. Optimum UHPFRC layer mix design and Properties





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After successfully meeting the required project targets, further optimization was carried out to enhance workability. This involved increasing the water-to-binder (w/b) ratio to 0.21 and incorporating higher quantities of superplasticizer, to classify the mixture as a self-compacting UHPFRC (SCC). Both mixtures' design details can be found in Table 3.

Constituent	Steel Fibers 2%	Steel Fibers 2% & PVA 1%
Constituent	Content (kg/m ³)	Content (kg/m ³)
Cement	880	880
Microsilica	220	220
Reference Sand	833	833
Water	231	231
Superplasticizer	67	67
Steel fibers 6mm	80	80
Steel fibers 13mm	80	80
PVA fibers	-	13
Water/Binder	0.21	0.21

 Table 3: SCC Mixture Constituents.

Results from compressive and flexural tests are illustrated in Figure 4 and Figure 5. It was observed that for formulations with 2% steel fiber content, alterations in the w/b ratio and compaction method did not have a significant impact on compressive and flexural strength results; however, a different behaviour was observed when PVA fibers were incorporated to the formulations. Specifically, the inclusion of PVA fibers led to a decrease of 16.51% and 18.43% in the compressive and flexural strength, respectively. These results are complemented by the stress-strain curves of Figure 6 and Figure 7 attained from compressive and direct tension tests.









Figure 4. 14-day and 28-day Compressive strengths of (a) mixture containing 2% steel fibers at w/b of 0.16 (•) and SCC with 2% steel fibers at w/b of 0.21 (+) and (b) and mixture containing 2% steel fibers (1:1) and 1% PVA at w/b of 0.16 (•) and SCC with 2% steel fibers (1:1) and 1% PVA at w/b of 0.21(+).



Figure 5. 28-day Flexural strength of mixture containing 2% steel fibers (•) and mixture containing 2% steel fibers and 1% PVA (+), each at w/b ratios of 0.16 and 0.21 (SCC).











Figure 6. Stress-Strain relationship from compressive strength tests on cylinders.



Figure 7. Stress-Strain relationship from tensile strength tests on beams.







3. Design and Development of the Fire-Resistant Geopolymer (FRG) Layer

3.1 Optimization of materials

The Fire-Resistant Geopolymer (FRG) material, which is the fire protective layer of the innovative Hybrid Laminated Material (HLM) for buildings and structures was designed and developed by partner FRC (Frederick Research Center), in collaboration with UCY and RECS. The development of this material was based on industrial by-products (wastes), specifically on fly ash (FA) and ground granulated blast furnace slag (GGBFS), thus decreasing the total production cost of the HLM and enhancing its sustainability. The optimization of FRG was performed through the study of the basic parameters of the geopolymerization process, including the composition of the geopolymer precursor (mix of solid raw materials), the solid-to-liquid (S/L) ratio, the alkali-metal used in the alkaline activator and the concentration of the alkali-hydroxide solution, the molar ratio of alkali-to-silicon oxides in geopolymer system and the curing time. All the developed geopolymer materials were evaluated in terms of density and compressive strength, while the optimized among them were also assessed for their fire resistance, through testing for thermal stability and mechanical performance at high temperatures, similar to those developed in a fire event.

Table 4 summarizes the chemical composition of the solid materials used in the geopolymer precursor. Both solid materials are already imported and available in Cyprus for the cement industry. In the frame of BAM project, these materials were used for the development of the FRG materials, without any further pre-treatment.

Oxide	FA	GGBFS
Na ₂ O	1.21	1.11
MgO	2.48	7.02
Al_2O_3	27.41	8.80
SiO_2	52.69	36.83
K ₂ O	2.71	0.31
CaO	2.47	44.67
TiO ₂	0.87	0.59
Fe_2O_3	7.51	0.45
LoI	2.36	-
Others		0.15
TOTAL	99. 72	99.93

Table 4: Chemical composition of solid materials used in the geopolymer precursor.





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The basicity (k_b) is a very important property of slags and indicates the weight ratio of basic oxides (CaO and MgO) to acidic oxides (SiO₂ and Al₂O₃) contained in a slag. If the basicity of a slag is greater than one, the slag is referred to as "basic"; in the opposite case, it is referred to as acidic. In general, the increase of slag basicity increases the cementitious properties of that slag. The GGBFS used in this investigation is a basic slag, with increased basicity $k_b = 1.13$. This slag is also considered suitable for alkali activation, since its reactivity expressed with the "simple basicity index" CaO/SiO₂ (1.21) is between 0.5 - 2, while its modulus of activity Al₂O₃ / SiO₂ (0.24) is between 0.1 and 0.6 ⁽¹⁾.

In Table 5, the chemical composition of sodium and potassium metasilicate solutions used in the alkali-activators of geopolymers is given. In addition, sodium and potassium hydroxide solutions, which were prepared by dissolving KOH or NaOH anhydrous pellets of analytical grade in distilled water, were used in geopolymers as alkali-activators. Both the alkali-hydroxide solutions were prepared at least 24 hours before the synthesis of the geopolymer samples.

able 5: Chemical composition of silicate solutions used in the alkali-activator				
Sodium silicate soluti	on (% wt.)	Potassium silicate solution	e (% wt.)	
SiO_2	28	SiO ₂	27	
Na ₂ O	7	K_2O	13	
H ₂ O	65	H_2O	60	
Density (g/mL)	1.346	Density (g/mL)	1.4	

Except of the alkali-silicate solutions, commercial silica fume (SF) provided by the Norwegian company ELKEM ASA was also used to improve the molar ratio of silicon-to-alkali oxides in the developed FRG materials. SF contains 95.3% wt. SiO2 with low content of FeO (2.37% wt.) and traces of K₂O and MgO.

The investigation of process parameters to optimize the FRG layer of the HLM includes six series of experiments. Table 6 summarizes the experimental conditions and the value range of the investigated parameters of the performed tests' series.

¹ F. Winnefeld et al., Influence of slag composition on the hydration of alkali-activated slags, Journal of Sustainable Cement Based Materials, 2015, 4 (2), pp. 85-100.







Tests Series	FA ⁽¹⁾ /BFS ⁽²⁾ (weight ratio in the precursor)	S/L (g/mL)	A ⁽³⁾	[AOH] ⁽³⁾ (mol/L, M)	SF (% wt. in the precursor)	SiO2/A2O ⁽³⁾ (molar ratio)
EXP 1	100 / 0 90 / 10 70 / 30 50 / 50	2.8	Na	7	0	0.774
EXP 2	90 / 10	2.8 3.8	Na	7	0	0.774
EXP 3	90 / 10	3.8	Na	4 5 7 8 10	1	1.205 1.018 0.775 0.694 0.580
EXP 4	90 / 10	3.8	K	4 5 7 8 10	1	0.842 0.711 0.541 0.485 0.405
EXP 5	90 / 10	3.8	Na	7	0	0.556 0.775 0.838 0.911 0.944
EXP 6	90 / 10	3.8	Na	7	0 1 2.5 5 10 15	0.775 0.948 1.210 1.645 2.515 3.385

Table 6: Experimental conditions of the performed tests series (EXP1 – EXP6).

Abbreviations: ⁽¹⁾ FA = Fly ash; ⁽²⁾ BFS = Ground granulated blast-furnace slag; ⁽³⁾ A = alkali-metal, Na or K.

In Figures 8-10, the effect of the studied geopolymerization process parameters on the compressive strength and density of the produced FRG materials is illustrated.







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Figure 9. Effect of the alkali-metal concentration in the alkaline activator (expressed as the concentration of NaOH or KOH solution for constant volumetric ratio of alkali-silicate to alkali-hydroxide solutions) on the compressive strength of FRG materials (curing conditions: T = 30 °C, t = 7 days).



Figure 10. Effect of the sodium-to-silicon oxides molar ratio in geopolymer matrix on the compressive strength of FRG materials (curing conditions: T = 30 °C, t = 7 days).

According to the results presented in Figure 8(a), the addition of GGBFS in the geopolymer precursor did not significantly improve the compressive strength of the materials. The FRG materials produced by 100% FA (0% GGBFS) developed compressive strength equal to 17.73 MPa, while those made with a weight ratio of FA/GGBFS = 50/50 presented a compressive strength of 16.83 MPa. However, the compressive strength values may not reflect the true strength of the materials, since the increase of GGBFS content in the geopolymer precursor resulted in plastic materials, which were prone to deformation under load without breaking (disruption of cohesion). Moreover, the increase of GGBFS content in the precursor led to materials with extensive surface cracking and increased shrinkage. The plastic behavior the FRG samples with FA/GGBFS weight ratio of 50/50 exhibited during compressive strength testing is shown in Figure







11(a), while Figure 11(b) shows the typical conchoidal fracture of the FRG samples with FA/GGBFS weight ratio of 90/10, after compressive strength testing.

The increase of solid-to-liquid (S/L) ratio (decrease of water content in the geopolymer paste) improved the materials' compressive strength.



Figure 11. (a) Plastic behavior and (b) typical behavior of specimens of the FA-based FRG materials with high and low GGBFS content, respectively, during compressive strength testing.

According to Figure 9, both alkaline activators resulted in FRG materials with similar compressive strength, ranging from 12 to 22 MPa, regardless of the type of the alkali-metal used. However, the highest compressive strength (22 MPa) was achieved in the Na-based alkaline activator geopolymer system, for the material prepared with 7M solution. Similar compressive strength (20 MPa) was also achieved for the K-based alkaline activator geopolymer system, with 4M solution.

The FRG materials also achieved a compressive strength of 22 to 25 MPa with a sodium-to-silicon oxides (Na_2O/SiO_2) molar ratio of approximately 1.3 (Figure 10), corresponding to a 7M NaOH solution concentration. This result was consistent regardless of the source of the dissolved silicates used in the geopolymer system, whether it was sodium silicate solution or silica fume.

However, the specimens produced with silica fume content higher that 1% wt. presented swelling phenomena during their curing procedure (Figure 12) and extensive surface cracking after curing, which both adversely affected the compressive strength of the materials. Specifically, the compressive strength of the FRG materials prepared with MS content $\geq 2.5\%$ wt. in the precursor decreased sharply. As it was observed during the samples' preparation, addition of MS content $\geq 2.5\%$ wt. caused foaming of geopolymers due to the hydrogen gas generated in the paste, through the reaction of metallic silicon contained in silica fume with water in strongly alkaline environment ⁽²⁾. Silica fume is a byproduct of the silicon and ferro-silicon industrial production, after the

² S.E. Abo Sawan et al., In-situ formation of geopolymer foams through addition of silica fume: Preparation and sinterability, Mater. Chem. Phys. 2020, 239, pp. 121998. <u>https://doi.org/10.1016/j.matchemphys.2019.121998</u>.







reduction of high-purity quartz by coal in electric furnaces and therefore, it has a high content of metallic silicon micro-particulates entrained in the furnace gases.





Based on the results shown in Figure 10, the optimum volumetric ratio of sodium silicate (SS) to sodium hydroxide (SH) solutions in the activator of FRG materials was 0.45 (v/v). Increasing the soluble silicate content in the activator, and thus in the geopolymer paste, decreased the paste's workability. This made casting difficult, as the stiff geopolymer paste hindered the formation of well-shaped cubic specimens. In general, a high concentration of soluble silicates in the geopolymer activator results in pastes that are difficult to handle and cast effectively.

In the frame of this investigation the curing temperature of materials was kept constant and equal to 30 °C, which can be considered as room temperature. Regarding the effect of curing time on the compressive strength of FRG materials, the samples cured for 28 days at 30 °C developed slightly increased compressive strength (about 2 - 3 MPa) comparing to those cured for 7 days at the same temperature. This observation confirms the well-established consideration regarding the high early developed compressive strength of geopolymers.

The above analysis of the results taken from the investigation of process parameters concluded to five optimized FRG materials that developed compressive strength higher than 20 MPa and apparent density around 1450 kg/m³, which could be used as the fire-resistant layer of the HLM developed in BAM project. However, one material among them is considered as optimum in this study (FRG-S1), developing the highest compressive strength of 25.39 MPa. Table 7 summarizes the synthesis and conditions, and the important geopolymerization ratios of the final optimum FRG material (FRG-S1). The synthesis and curing conditions, and geopolymerization ratios conditions of all the five optimized FRG materials are listed in Table 8 below.





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Synthesis Conditions				
Parameter	Value			
Mass of FA (g)	360			
Mass of GGBFS (g)	40			
Mass of SF (g)	0			
Volume of 7 M NaOH (mL)	72.4			
Molarity of NaOH solution (M)	7			
Volume of Na-silicate solution (mL)	32.6			
Ratio	Value			
[NaOH] in alkaline activator (M)	5.9			
S/L ratio (g/mL)	3.8			
SS/SH volumetric ratio (v/v)	0.45			
SiO ₂ /Na ₂ O molar ratio (Ms)	0.637			
Curing Conditions				
Parameter	Value			
Temperature (°C)	30			
Time (days)	7			

Table 7: Synthesis and curing conditions of the selected optimum FRG material (FRG-S1).







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	(FRG-S1)	(FRG-S2)	(FRG-S3)	(FRG-S4)	(FRG-S5)
Synthesis conditions			Value		
Mass of FA (g)	360	445.5	445.5	450	450
Mass of GGBFS (g)	40	49.5	49.5	50	50
Mass of SF (g)	0	5	5	0	0
Volume of 7 M NaOH (mL)	72.4	90.5	90.5	100.5	82
Molarity of NaOH solution (M)	7	7		7	7
Molarity of KOH solution (M)			4		
V of Na-silicate solution (mL)	32.6	40.75		30.75	49.25
V of K-silicate solution (mL)			40.75		
Ratios			Value		
FA/GGBFS mass ratio	90 / 10	90 / 10	90 / 10	90 / 10	90 / 10
Silica Fume (%wt.)	0	1	1	0	0
[NaOH] in alkaline activator	5.91	5.91	3.84	6.17	5.68
S/L ratio (g/mL)	3.8	3.8	3.8	3.8	3.8
SS/SH volumetric ratio (v/v)	0.45	0.45	0.45	0.31	0.6
SiO ₂ /Na ₂ O molar ratio (Ms)	0.637	0.637	0.98	0.611	1.801
Curing conditions			Value		
Temperature (°C)	30	30	30	30	30
Time (days)	7	7	7	7	7
Compressive Strength (MPa)	25.39	22.02	20.35	20.36	22.05

Table 8: Synthesis and curing conditions of the five optimized FRG materials.



The project is implemented under the programme of social cohesion "THALIA 2021-2027" co-funded by the European Union, through Research and Innovation Foundation.



3.2 Thermal and Mechanical Stability of FRG Materials at High Temperatures The optimum material from each alkali-activator system, Na and K, which are coded in Table 4 as FRG-S1 and FRG-S3 respectively, were subjected to a thermal treatment test, as a preliminary assessment of their fire resistance. According to this test, the FRG samples were heated for 2 hours at the temperatures of 600, 800 and 1050 °C, using the electric furnace shown in Figure 13. The tested materials were cured at 30 °C for 7 days and left for hardening at ambient temperature for at least one month.



Figure 13. The electric furnace was used for the fire resistance assessment testing of FRG materials.

In each thermal treatment test, three cubic samples with dimensions 50x50x50 cm³ were placed in the furnace and heated with a constant heating rate of 4.4 °C/min until the desired temperature (600, 800 or 1050 °C), in which they remained for 2 hours. Then, the specimens were removed from the furnace and allowed for cooling down to room temperature in open air conditions, before any measurement or testing. After each thermal test, the materials compressive strength, mass loss, density and linear shrinkage were measured, while their structural coherence was macroscopically observed, as well. In Figure 5, the compressive strengths of the optimum Na- and K-based FRG materials tested at high temperatures for 2 hours are plotted versus the exposure temperature. These optimum Na-FRG and K-FRG materials are coded in Table 7 as FRG-S1 and FRG-S3, respectively.



Figure 14. Compressive strength of the optimized FRG-S1 (Na-FRG) and FRG-S3 (K-FRG) materials after exposure to high temperatures for 2 hours (experimental conditions are given in Table 7).





As shown in Figure 14, the trend shown by the compressive strength variation with temperature in the case of the Na-FRG material is opposite to the corresponding trend of the K-FRG material. The compressive strength of Na-FRG increased remarkably after the material exposure to 600 °C and then, it was slightly reduced with the temperature increasing up to 800 °C and sharply reduced to approximately its initial value, after the material's exposure to 1050 °C. The compressive strength of K-FRG was sharply reduced after been exposed to 600 °C and then increased with the increase of temperature, up to 1050 °C. The evaluated properties of Na-FRG and K-FRG materials after their exposure to elevated temperatures for 2 hours, are presented in Table 9.

Material ID	Temperature (°C)	Density (kg/m ³)	Mass loss (% wt.)	Linear Shrinkage (%)
	30	1467		
Na-FRG	600	1432	7.5	1.2
	800	1373	8.4	1.1
	1050	1381	9.3	1.5
	30	1462		
K-FRG	600	1364	6.2	1.0
	800	1394	7.2	0.6
	1050	1463	7.5	1.8

Table 9: Properties of the Na-FRG and K-FRG materials after exposure to high temperatures.

No cracks or any other sign of spalling or deformation were visible on both Na-FRG and K-FRG samples after their exposure to 600 °C. At the temperature of 800 °C, a few surface-microcracks appeared, which disappeared at 1050 °C, due to sintering phenomena taking place in geopolymers when exposed at temperatures higher than 950 °C ⁽³⁾. Based on the experimental results of the FRG materials fire resistance assessment, the Na-FRG material was selected for further validation, as the most appropriate fire-resistant layer of the developed HLM.

³ M. Lahoti et al., Effect of alkali cation type on strength endurance of fly ash geopolymers subject to high temperature exposure, Mater. Des. 2018, 154, pp. 8–18. https://doi.org/10.1016/j.matdes.2018.05.023.







4. Pull-Off Testing – Hybrid Laminated Material (HLM)

The goal of this report is to detail the experimental results and findings of a pull-of test on a composite material conducted according to EN 1542. The adhesion strength and surface type between a fire-resistant geopolymer and an Ultra High-Performance Fibre Reinforced Concrete material with blast and impact characteristics were evaluated. The utilization of a direct pull-off method determined the maximum force at failure and the type of failure.

4.1 Hybrid Laminated Material (HLM)

The examined material consists of two layers designed to provide distinct characteristics to the composite end product: i.e., an Ultra High-Performance Fiber Reinforced Concrete (UHPFRC) Layer which provides blast and impact resistance characteristics and a fire-resistant geopolymer (FRG) Layer. Both materials were studied, developed and presented in "D3.1 – Design and Development of Hybrid Laminated Material (HLM)". The synthesis for each layer is presented in Tables 10 and 11, respectively.

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Synthesis Conditions	FRG Layer
S/L (kg/L)	3.80
SS/SH	0.45
Alkaline Solution Type	NaOH (7M)
Alkaline Solution Quantity (gr)	41
Na ₂ SiO ₃ xH ₂ O (SS) (ml)	91
FlyAsh-90 (gr)	450
GGBFS-10 (gr)	50

 Table 11: Synthesis of the ultra-high-performance fiber reinforced concrete.

Constituent (kg/m ³)	UHPFRC Layer
Cement	880
Microsilica	220
Reference Sand	833
Water	172
Superplasticizer	67
Steel Fibers 6 mm (1%)	80
Steel Fibers 13 mm (1%)	80
PVA Fibers	13
Water/Binder (w/b)	0.16





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4.2 Test Procedure

4.2.1 Specimen Preparation

For the experimental procedure, three different setting phases were considered to investigate the adhesion properties of the HLM material. The first phase involved casting the fresh FRG paste onto the fresh UHPFRC layer (Fresh-on-Fresh). In the second and third phases, after the UHPFRC layer had set, a smooth (Fresh-on-Smooth) and a roughened (Fresh-on-Rough) surface were utilized, respectively. The preparation timeline of the HLM specimens depended on the type of setting phase.

Initially, the UHPFRC mixture was cast according to the design in Table 2. However, steel fibers were excluded from the UHPFRC mixture to facilitate the drilling process. This exclusion represents a conservative scenario for the pull-off maximum force, possibly resulting in lower adhesion values than the actual experimental results.

After casting the UHPFRC layer, the FRG paste was prepared and poured into the mould for the Fresh-on-Fresh specimens. For the Fresh-on-Rough specimens, the surface of the UHPFRC was roughened with a metallic brush to enhance adhesion between the two materials. Fresh-on-Smooth specimens were completely hardened, and the following day, an FRG layer was cast on top of the previously set UHPFRC material.

A total of 15 specimens were prepared with average dimensions of 150 mm x 150 mm x 80 mm for the HLM material, corresponding to 150 mm x 150 mm x 30 mm for the FRG material and 150 mm x 150 mm x 50 mm for the UHPFRC material.

4.2.2 Bonding Agent – Alternative Options

The direct application of the FRG material on the UHPFRC layer aimed to assess the adhesion properties of the HLM end-product when cast directly with varying surface roughness and without additional support methods (e.g., fire-resistant anchors or chemical bonding agents). The effectiveness of using anchors (Fischer FNA 6x30/30 A4 stainless steel) or fire-resistant adhesive epoxy resin (Sikaflex by Sika Ltd) has been documented in similar geopolymerized composite materials developed by the same research team and reported in relevant literature. Therefore, a minimum adhesion strength of 2 MPa was targeted using these simple layer-to-layer adhesion methods. If this minimum strength cannot be achieved with the simple method, then the successful development of the HLM and a strong bond between the layers can be ensured using alternative methods, as previously demonstrated.





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4.2.3 Test Procedure Overview:

The test procedure for measuring the tensile bond strength between the FRG and UHPFRC is illustrated in Figure 1 and is prescribed in the following steps:

1) <u>Defining the dimensions of the testing area</u>: A 62 mm core drilling device was utilized to core drill through the surface of the HLM repair product.

2) <u>Fixing the dolly:</u> A dolly was fixed using a thin layer of epoxy resin adhesive to the surface of the HLM composite. The quantity of epoxy was sufficient to cover the entire surface of the dolly without penetrating the clearance drilled by the core drilled.

3) <u>Pull-off Test Equipment</u>: A pull-off test device with an attached measurement device to record the exerted force was concentrically attached over the dolly. The equipment had the pulling capacity to cause tensile bond failure of the specimen.

4) <u>Applying the load</u>: A continuous and even load was applied at a rate of 0.05 ± 0.01 MPa/S, until failure occurred. It was ensured that no significant fluctuation occurred in the applied load, as it was applied manually.

5) <u>Recording the results:</u> The maximum force at failure and the type of failure between the two composite layers were recorded.



Figure 15. Pull-off test procedure overview.





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4.3 Results

4.3.1 Maximum Force

Table 12 presents the maximum force recorded for each specimen after applying a pressure of 0.05 \pm 0.01 MPa/s. Notably, four specimens (two from the Fresh-on-Fresh and two from the Fresh-on-Smooth) detached during the core drilling process. The Fresh-on-Smooth specimens exhibited the weakest bonding between the two layers, with one of the three specimens not registering any measurement on the device.

In contrast, the Fresh-on-Fresh and Fresh-on-Rough specimens showed better adhesion, with maximum forces of 1.00 kN and 1.10 kN, respectively. However, none of the three surface adhesion types achieved the targeted adhesion strength of 2 MPa.

	Fresh-on-Fresh	Fresh-on-Smooth	Fresh-on-Rough
1	1.30	N/A	1.00
2	0.40	0.30	1.40
3	1.20	0.40	1.20
4	-	-	0.68
5	-	-	1.10
Average	1.00 kN	0.35 kN	1.10 kN

Table 12: Maximum Force on each surface type of HLM specimen.

4.3.2 Failure Modes

Out of the fifteen specimens tested, four detached during the core drilling process. None of the remaining specimens experienced cohesive failure of the substrate; instead, failure occurred at the bond interface between the two layers. This indicated that the tensile bond strength at the interface was weaker than the cohesive strength of each individual layer. Figure 2 illustrates the failure modes of all specimens across all adhesion surface types.



Figure 16. Failure types for HLM specimens from top to bottom: Fresh-on-Fresh, Fresh-on-Smooth, Fresh-on-Rough.





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After evaluating the results, it was decided to use fire-resistant adhesive epoxy resin (Sikaflex by Sika Ltd) to bond the two layers (UHPFRC and FRG) of the HLM, as this method has been successfully implemented in similar cases in the past. This adhesive bond exceeded the targeted value of 2 MPa, causing failure to occur in the weaker of the two layers, which was the fire-resistant geopolymer. Sikaflex adhesive is well-suited for this specific application, since during high temperature testing, the adhesive did not melt. This adhesive provides a clean and seamless attachment method, leaving no visible fasteners or marks, and its application is user-friendly and straightforward. The adhesive is known for its versatility and compatibility with a wide range of construction materials, combining durability and flexibility. These characteristics are crucial for attaching protective materials to surfaces subject to environmental conditions and structural movements. Additionally, the specific adhesive is a cost-effective solution compared to other methods that might require specialized fasteners or additional labour expenses.





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5. Conclusions

The development of the blast- and impact-resistant layer of the HLM revealed the following conclusions:

- The UHPFRC layer of the HLM was developed as an optimized version of a previously created material by the research team. Various mix differentiations were examined before concluding that formulations containing 2% steel and 1% PVA fibres, along with the replacement of local sand with standard silica sand, were selected as the most cost effective that met the project's minimum strength requirements. In addition, a self-compacting version of the 2% steel and 1% PVA UHSC was developed, which exhibited a 16.51% decrease on compressive strength, and 18.43% decrease on flexural strength.
- Importantly, when no PVA fibres were included, the 2% steel fibre USHC layer did not reach the BAM project strength requirements. The self-compacting version of this mix did not exhibit significant disparity in terms of strength, compared to its non-self-compacting equivalent.

Based on the optimization study of geopolymer materials for use as the fire-resistant layer (FRG) of the HLM and their fire-resistance assessment, the following conclusions are drawn:

- The compressive strength of the FA-based geopolymers developed in this study was significantly affected by the S/L ratio and the concentration of the alkali hydroxide solution used in the activator. An S/L ratio equal to 3.8 g/mL was proved to be optimal for FRG materials, with 7M NaOH and 4M KOH solutions proving optimal for the corresponding alkaliactivators.
- The type of alkali-activator and the addition of GGBFS to the geopolymer precursor did not substantially affect the compressive strength of materials. However, the addition of GGBFS significantly increased the materials' apparent density from 1410 to 1710 kg/m³. An optimal FA to GGBFS mass ratio of 90:10 was identified for the developed materials.
- The optimal curing time for FRG materials is 7 days, since they develop around 85-98% of their 28-day compressive strength within this period.
- The addition of soluble silicates in the FRG materials improved their compressive strength, regardless of the silicate source (i.e., alkali-silicate solution or silica fume). However, adding silica fume amounts ≥ 2.5% wt. resulted in the reduction of materials' compressive strength, due to foaming caused by the hydrogen gas release. This gas was released in geopolymer pastes as a product of the reaction between metal-silicon and water in strong alkaline conditions.







Increasing the volumetric ratio of sodium silicate (SS) to sodium hydroxide (SH) solutions by beyond 0.8 also inhibited the workability of geopolymer pastes. Optimization of the FRG materials was achieved for a molar ratio of Na_2O/SiO_2 around 0.95 for SF addition and around 0.85 for SS solution.

- The optimum Na-FRG and K-FRG materials showed different behaviors at high temperatures. The compressive strength of Na-FRG increased significantly after exposure to 600 °C and then decreased up to 1050 °C, while the compressive strength of K-FRG was sharply decreased after exposure to 600 °C and then increased up to 1050 °C. The variations of density and linear shrinkage with temperature were negligible, while the mass loss of the Na-FRG material was higher than that of the K-FRG one after materials' exposure to high temperatures.
- The Na-FRG material, which exhibited the highest compressive strength (25.39 MPa), was selected as the optimal fire-resistant layer for the HLM. This material was synthesized with a mass ratio of FA/BFS = 90/10, Na-based activator with [NaOH] = 7M and SS to HS volumetric ratio of 0.45 in the activator, no SF content and S/L ratio = 3.8 g/mL.

Regarding the bond between the FRG and UHPFRC layers:

- The adhesion bond achieved between the FRG and UHPFRC with the use of geopolymeric paste did not meet the minimum requirements for the tensile bonding strength of 2 MPa. Therefore, it was decided to use a fire-resistant adhesive epoxy resin to bond the two layers of the HLM, as this method has been successfully implemented in similar cases in the past. This adhesive bond exceeded the targeted value, causing failure to occur in the weaker of the two layers, which was the fire-resistant geopolymer.





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