

1 Fire Performance of Solid Aluminium of Composite Cladding 2 Panels Incorporating Intumescent Coatings

3 Touha Nazrun¹, Md Kamrul Hassan^{1,*}, Md Rayhan Hasnat¹, Md Delwar Hossain¹, Swapan
4 Saha¹

5 ¹ School of Engineering, Design and Built Environment, Western Sydney University, Penrith, NSW
6 2751, Australia;

7 8 **Abstract**

9 The use of solid aluminium as the outer layer of aluminium composite panels (ACP) has raised concerns
10 about fire safety in high-rise buildings. Solid aluminium begins to melt at approximately 660°C, which
11 can exacerbate fire hazards by transferring significant heat from the fire exposed to unexposed sides.
12 This research investigates the fire performance of solid aluminium when treated with two different
13 intumescent coatings (Coating-A and B). The study evaluates solid aluminium with/without coatings to
14 determine their effectiveness in mitigating fire risks. Comprehensive analysis for material
15 characterisation and fire test were conducted to assess the microstructure, elemental composition, and
16 thermal degradation and fire behaviour of the coatings. The findings reveal that while solid aluminium
17 presents significant fire risks when exposed to high temperatures, intumescent coatings can
18 substantially improve fire resistance of solid aluminium. Coating-A, when applied to both sides of the
19 aluminium, reduces melting but still allows some flame spread. In contrast, Coating-B provides
20 exceptional fire protection, preventing melting and flame spread when applied to one side. However,
21 the potential hazard of airborne char particles from Coating-B is the key issue. These results underscore
22 the effectiveness of intumescent coatings to enhance fire safety in solid aluminium cladding.

23 **Keywords:** Intumescent coatings, Fire safety, Solid aluminium panels, Aluminium composite panels.
24

25 *Correspondence: k.hassan@westernsydney.edu.au

26 **1. INTRODUCTION**

27 The use of advanced lightweight materials, such as aluminium composite panels (ACP),
28 polymers, and fibre-reinforced composites, has increased in exterior cladding systems due to

29 their excellent thermal insulation, weather resistance, and aesthetic finishes. However, these
30 lightweight materials are flammable and pose significant fire risks to human life, the
31 environment and the economy [1-3]. In recent years, several fire incidents occurred involving
32 external cladding systems. For example, Injuries and deaths occurred as a result of fires in the
33 Milan tower block, Italy in 2021 [4], Neo 200 Building, Melbourne, Australia, in 2019 [5],
34 Dwelling Building, Jecheon, South Korea in 2017 [6], Marina Torch Tower, Dubai, UAE, in
35 2017 [7], Hotel The Address, Dubai, UAE, in 2016 [7], and Nasser Tower, Sharjah, UAE in
36 2015 [7]. The causes of these fires varied and included combustible ACP, flammable cladding,
37 and insulation [1-3, 8]. Fire protection for external cladding has become a critical global issue
38 [9]. There are two types of fire protection systems: active and passive fire protection. Active
39 fire protection includes detecting, controlling, and extinguishing fires. This system can be used
40 for both automatic fire alarms and fire detectors, as well as manual fire extinguishers and
41 hydrant boxes [10, 11]. On the other hand, passive fire protection involves materials that can
42 withstand high temperatures without losing mechanical strength, such as intumescent coating
43 materials that help prevent and ensure safe evacuation by providing fire resistance [12].

44 Solid aluminium is a highly sustainable metal due to its recyclability, durability, and
45 energy efficiency, which is widely used in ACP panels. With a long lifespan of 30 to 50 years,
46 its resistance to weather and corrosion ensures low maintenance costs. These qualities make it
47 an excellent choice for a wide range of applications in the building industry, including façades,
48 windows, and cladding [13]. Solid aluminium has a higher strength-to-weight ratio and offers
49 significant weight reduction due to its lightweight properties [13, 14]. However, solid
50 aluminium has a major drawback: it has a relatively low melting point of around 660 °C and
51 begins to lose its strength around 150°C [15]. Recent fire incidents in the UK, Australia, and
52 other countries have revealed that the solid aluminium used as outer layer in the ACP panels
53 significantly contributed to fire hazards in high-rise buildings [16-18]. Many research work

54 [19, 20] has been published to improve the fire performance of the core materials of ACP
55 panels. Additionally, much research successfully improved the fire performance of core
56 materials of ACP panels [21]. However, a limited research study is conducted to improve the
57 melting issue of the solid aluminium used as outer skin in the ACP panels. Intumescent coatings
58 can be a highly recommended and effective solution for safeguarding aluminium against fire
59 incidents, providing a valuable protective measure.

60 Intumescent coatings are fire-retardant paints which react under fire exposure and
61 significantly expand many times to their original thickness in a controlled manner by negating
62 the carbonaceous char. The thick layer of insulating carbonaceous char protects the substrate
63 material from fire damage. Additionally, it helps to provide additional time for occupants to
64 escape safely in a fire incident by trapping fire and smoke [22]. The thick char layer has low
65 thermal conductivity and acts as a thermal insulator during the fire, which helps to prevent a
66 significant temperature rise to the fire-exposed and unexposed sides and protects the structure
67 from collapsing [23]. Intumescent coatings are formulated with three major components:
68 ammonium polyphosphate (APP), which acts as the acid source; pentaerythritol (PER), which
69 serves as the carbon source; and melamine (MEL), functions as the blowing agent. This process
70 produces carbonaceous and phosphocarbonaceous residues, leading to the formation of a char
71 layer [24, 25].

72 Intumescent coatings have a diverse application on steel [26], wood [27, 28], timber
73 [29] and concrete materials [30, 31], yet their application on the outer layer of ACP has not
74 been explored. The melting of the outer layer of ACP is a common issue nowadays. The char
75 of intumescent coating can protect aluminium on the outer surface of ACP panels when
76 exposed to fire. However, selecting the appropriate coating for application is a big challenge
77 due to the diversity of available commercial products. They are different from each other in
78 their chemical composition, application methods, and levels of fire protection. Additionally,

79 their effectiveness can vary significantly based on the specific conditions of a fire. Therefore,
80 a proper investigation is needed in the field of fire protection by addressing the overlooked
81 issue of solid aluminium melting in ACPs, proposing intumescent coatings as a viable solution
82 for improving the fire resistance of solid aluminium skin used in the composite cladding panels.

83 To address the above issues, this study focuses on exploring the fire behaviour of solid
84 aluminium coated with two distinct types of intumescent coatings, each with different chemical
85 compositions and fire performance characteristics. This research paper aims to investigate the
86 influence of these coatings on char formation and their ability to provide fire protection to solid
87 aluminium skin used in ACPs under fire conditions of 1000°C and offer insights into their
88 potential application for enhancing fire safety in building cladding systems.

89 **2. EXPERIMENTAL DETAILS**

90 **2.1 Test specimens**

91 In this study, solid aluminium panels with and without intumescent coating have been
92 investigated experimentally. A total of 8 test specimens for three different categories of solid
93 aluminium panels with and without applying coating tests were prepared in this study to
94 conduct the fire tests. Each specimen was cut into the dimensions of 200 mm × 200 mm. Two
95 distinct water-borne fire-retardant coatings were purchased from commercial sources to apply
96 the coating on the solid aluminium panels. These two coatings are introduced in this study as
97 Coating-A and Coating-B. These coatings are referred to as non-toxic and non-hazardous fire-
98 retardant coatings by their respective manufacturers. The thickness of the solid aluminium for
99 all specimens was considered 0.5 mm thick because this thickness is widely used as the outer
100 skin of aluminium composite panels (ACP). In the first category, two specimens were prepared
101 without applying the intumescent coating (SP-C-0), see **Table 1**. In the second category, two
102 specimens were prepared to investigate the effect of Coating-A applied on one side of the panel
103 (SP-C-A). In the third category, two specimens were prepared for Coating-B applied on one

104 side of the panel (SP-C-B). In the fourth category, another two specimens were prepared for
 105 Coating-A(SP-C-A-D) to investigate the effect of Coating-A on both sides. The measured
 106 thicknesses of applying Coating-A and B are reported in **Table 1**. It is worth noting that the
 107 surfaces of the solid aluminium were cleaned and dried properly before applying both coatings.
 108 After the completion of the coatings being applied to the aluminium panels, a drying period of
 109 four days was ensured for the coatings to dry completely.

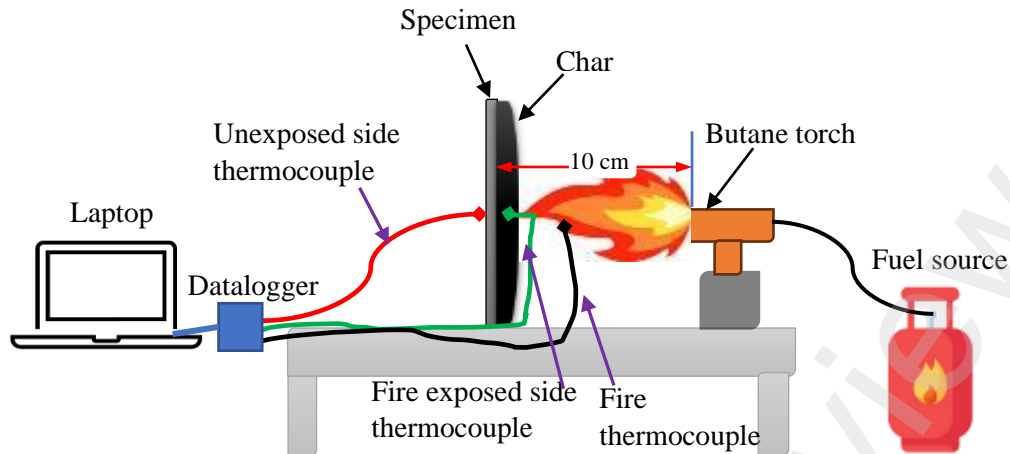
110 **Table 1** Test specimen details of solid aluminium panels with and without coating

Sample Category	Sample label	Dimension (width × depth)	Total thickness	Coating type	Coating thickness	No of specimens
Category 1	SP-C-0	200 × 200	0.5	-	-	2
Category 2	SP-C-A	200 × 200	1.5	A	1.0	2
Category 3	SP-C-B	200 × 200	1.5	B	1.0	2
Category 4	SP-C-A-D	200 × 200	2.0	A	1.5 (1+0.5)	2

111

112 2.2 Fire testing using Butane Torch

113 The butane torch test was employed to evaluate the fire performance of Coating-A and
 114 B on the aluminium panel. Natural gas was used as a fuel in this test, and the test was performed
 115 in an open environment. Three K-type thermocouples were used to monitor the temperatures
 116 of the fire, the front surface of the sample (i.e., fire-exposed side), and the back surface of the
 117 sample (i.e., fire unexposed side), see **Figure. 1**. The temperature readings of each
 118 thermocouple were recorded at every one-second time interval using a data logger connected
 119 to a laptop. Once the fire temperature reached around 1000 °C, the fire temperature was kept
 120 constant for the remaining testing time. It is worth mentioning that each specimen was placed
 121 at an identical distance from the torch, which was 10 cm. Additionally, each coated sample was
 122 exposed to the flame for a standardised duration of 10 minutes, similar to previous research
 123 [32].



124

125 **Figure 1:** Test setup used for fire testing of solid aluminium with intumescent coating.

126 **2.3 Characterisation of intumescent coating and char**

127 **2.3.1 Thermogravimetric analysis**

128 Thermal degradation and mass loss of both coatings were investigated through
 129 thermogravimetric Analysis (TGA). The analysis was assessed by using a TGA instrument.
 130 The coating samples were heated with temperature from room temperature to 1000°C, at a rate
 131 of 10°C per minute under an air atmosphere.

132 **2.3.2 Scanning electron microscopy with EDS**

133 Scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDS)
 134 analysis was conducted to understand micro- and nanoparticle imaging characterisation of both
 135 coating materials. SEM (model JEOL 6510LV) with EDS detector analysed the coating
 136 samples before and after the fire test. The EDS working distance was 15mm. Using the SEM,
 137 500 µm, 100 µm, 50 µm and 10 µm images were taken of the coating samples.

138 **2.3.3 X-ray diffraction**

139 The mineralogical composition of the coating sample was identified by using X-ray
 140 diffraction (XRD) (2019 model). CuK α radiation was used to analyse the coating sample as the
 141 X-ray source. The analysis covered a 2 θ range of 5° to 90°. The instrument utilised a LynxEye

142 XE-T detector with a fixed slit size of 0. 20°. The instrument operated at 40kV and 40mA
143 power sources, and the run time was approximately 1 hour and 11 minutes.

144 **2.3.4 Fourier transform infrared spectroscopy**

145 Fourier Transform Infrared Spectroscopy (FTIR) spectra were obtained using a Bruker
146 Vertex 70 FTIR spectrometer, also from Germany. The spectra were collected using a Diamond
147 Attenuated Total Reflection (ATR) accessory with a resolution of 4 cm⁻¹, averaging 32 scans
148 per measurement. The spectral range covered was from 600 cm⁻¹ to 4000 cm⁻¹.

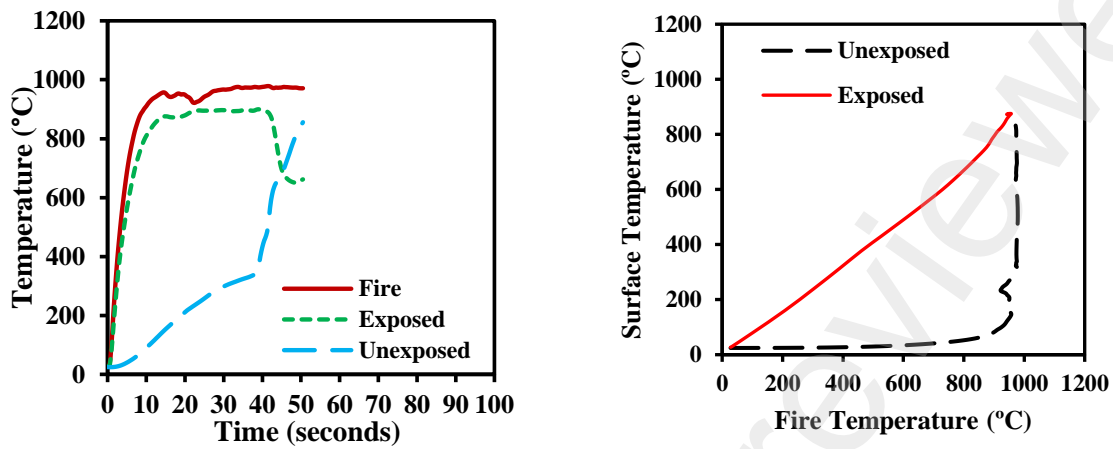
149 A 6 mm diameter of sample area was used for analysis, and the data were recorded in
150 absorbance units. To ensure accurate measurements, background correction was performed
151 before each new sample set to account for any environmental effects in the laboratory.

152 **3. RESULT & DISCUSSION**

153 **3.1 Temperature profile at fire exposed and unexposed sides of solid aluminium panel** 154 **without coating**

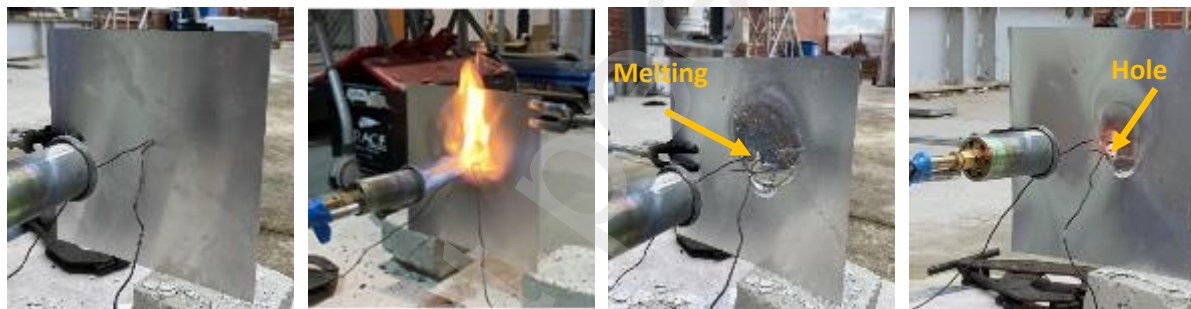
155 The fire behaviour of 0.5mm solid aluminium without coating (SP-C-0 specimen) was
156 investigated using a butane torch, and the temperature-time curves of fire, exposed and
157 unexposed sides of the SP-C-0 specimen, as shown in **Figure 2(a)**. It can be seen that the
158 temperature at the exposed side increases linearly with an increase in the fire temperatures until
159 872 °C. However, the temperature at the unexposed side does not increase linearly after the
160 temperature of the exposed side is 660°C. This could be due to the melting of aluminium at
161 660 °C. After melting solid aluminium, the temperature at the unexposed side increases non-
162 linearly until the fire temperature of 967 °C and then increases rapidly when the fire
163 temperature reaches around 970 °C, as shown in **Figure 2(b)**. This could be due to the rapid
164 onset of melting of aluminium and forming a hole on the centre of the specimen (**Figure 3**). It
165 can be noted that the melting areas of aluminium become like the ash of paper material burning.

166 This behaviour of aluminium is aligned with the previous research reported in the literature
 167 [33].



168 (a) Time vs temperature curves
 169 (b) Fire vs surfaces temperatures

170 **Figure 2:** Fire behaviour of SP-C-0 specimen without coating



171 (a) Before testing (b) During testing (c) Specimen melting (d) After testing

172 **Figure 3:** Photos of SP-C-0 specimen without coating during and after fire testing

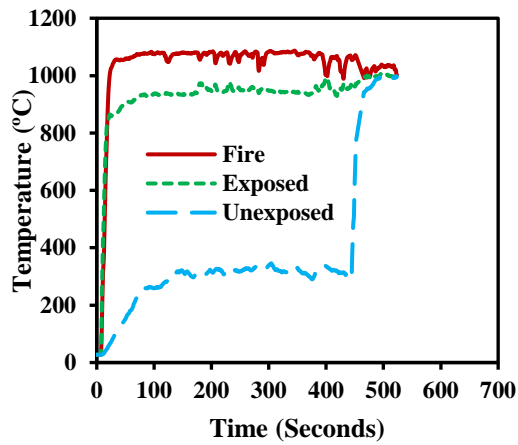
173 **3.2 Effect of Coating-A on the temperature profile at fire exposed and unexposed sides**
 174 **of solid aluminium panels**

175 Specimen SP-C-A and SP-C-A-D are coated with Coating-A. Each aluminium panel
 176 has a different thickness (see **Table 1**). As reported in the previous section, Specimen SP-C-A
 177 has one side coating on the fire-exposed side with a thickness of 1.0 mm, and specimen SP-C-
 178 A-D has both sides coating, fire-exposed side of 1.0 mm and unexposed side of 0.5 mm. The
 179 test results of the single-side and both sides coating are discussed below.

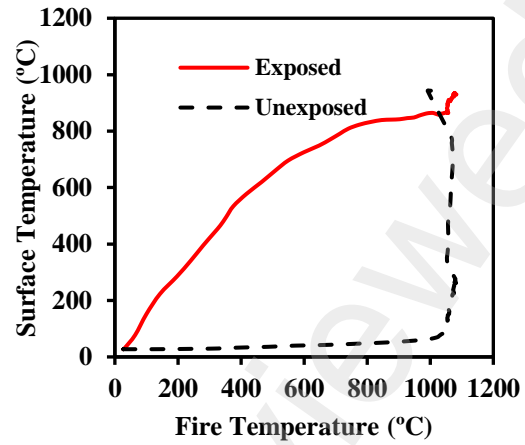
180 **(a) Coating-A applied on one side (fire exposure side)**

181 **Figure 4** shows the temperature profiles of SP-C-A. The measured temperature vs time
182 curves of fire, exposed side and unexposed side of specimen SP-C-A are presented in **Figure**
183 **4(a)**. In contrast, **Figure 4(b)** demonstrates the exposed and unexposed side's temperatures
184 against the fire temperature. It can be seen from **Figure 4(b)** that the temperature at the fire-
185 exposed side increases linearly with the increase in fire temperatures to 660°C. The temperature
186 at the exposed side is higher than the fire temperature until 800°C (**Figure 4(a)**). This could be
187 due to the ignition of the coating materials. It is worth noting that when fire is applied to the
188 sample SP-C-A, Coating-A ignites first and then burns for a period before giving protection,
189 see **Figure 5(b)**. The main reason for the burning of Coating-A is the presence of hydrocarbon
190 in Coating-A. This proves that after a certain period of fire exposure, the aluminium panel with
191 Coating-A becomes vulnerable due to the flame spreading vertically. After forming the char,
192 the exposed side temperature is lower than the fire temperature (**Figure 4(a)**). However, the
193 char did not protect the aluminium panel effectively from melting due to the thinner char layer,
194 see **Figure 5(c)**. As a result, the unexposed side temperature increases significantly until
195 1000°C and then increases rapidly, see **Figure 4(b)**. This could be due to the melting of solid
196 aluminium on the back side of the specimen, as seen in **Figure 5(d)**, and the occurrence of hole
197 formation during the experiment. The experiment had to be prematurely terminated due to the
198 occurrence of a hole in the sample. Based on this test, it can be concluded that the protection
199 capabilities of Coating-A applied on one side are very limited in time, and melting is still
200 observed as a key issue.

201



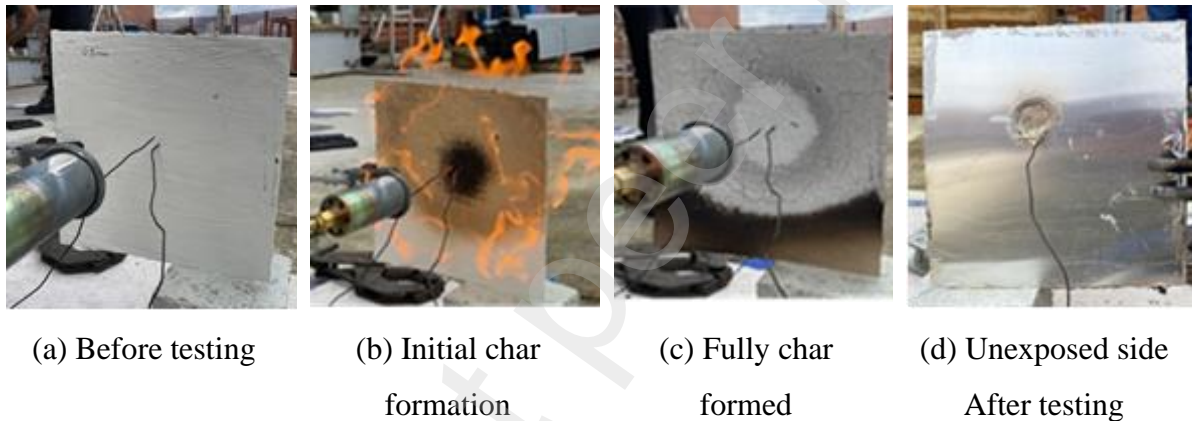
(a) Time vs temperature curve



(b) Fire vs surfaces temperature curve

Figure 4: Fire behaviour of SP-C-A specimen with one side Coating-A

202
203



(a) Before testing (b) Initial char formation (c) Fully char formed (d) Unexposed side After testing

Figure 5: Photos of tested specimen SP-C-A during and after fire testing

204

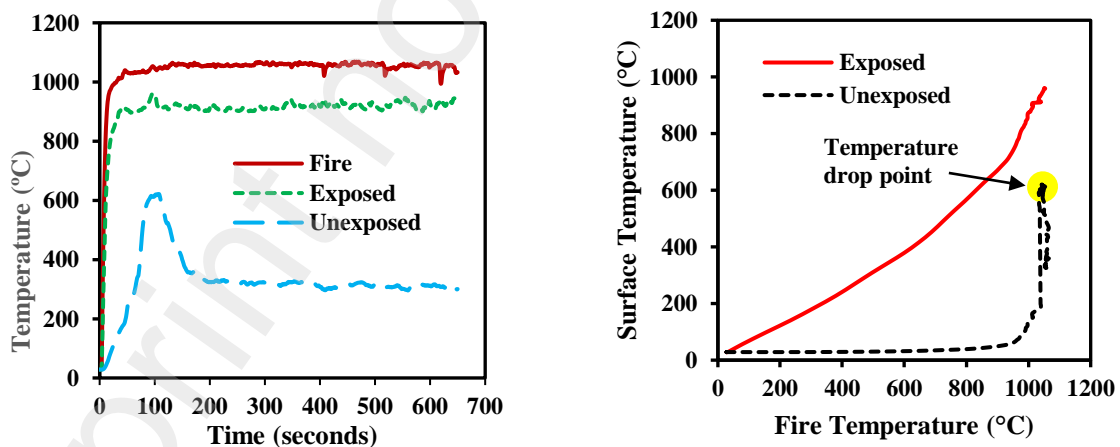
(b) Coating-A applied on both sides (fire exposed and unexposed sides)

205

206 The temperature profile of Coating-A applied on both sides of Specimen SP-C-A-D is
 207 reported in **Figure 6**. The coating thickness (1 mm) on the exposed side of SP-C-A-D is the
 208 same as that of the specimen SP-C-A. As a melting issue on the back side of SP-C-A was
 209 observed, 0.5 mm Coating-A was applied to the unexposed side of SP-C-A-D to check the
 210 effectiveness of Coating-A. The temperature profile with respect to the time of fire and exposed
 211 and unexposed sides of the SP-C-A-D specimen is shown in **Figure 6(a)**. **Figure 6(b)** shows
 212 fire temperature vs both surface temperature curves of the specimen SP-C-A-D. It can be
 213 observed that the temperature on the exposed side and unexposed side increases linearly until
 214 around 909 °C and 620 °C. When specimen SP-C-A-D is exposed to the fire, the coating

215 initially ignites similarly to the specimen SP-C-A. It burns temporarily on both sides (exposed
 216 and unexposed). This ignition and burning causes a rapid temperature increase on the
 217 unexposed side (as shown in **Figures 6(a-b)**). However, after the burning phase, the coating
 218 provides effective protection, leading to a subsequent temperature drop on the unexposed side,
 219 as shown in **Figures 6(a-b)**. **Figure 7(b)** indicates that the coating ignites before complete
 220 charring, and **Figure 7(c)** shows that no more flame spread was noticed on the coating after
 221 complete char formation. The Coating-A applied on both sides of the SP-C-A-D specimen
 222 successfully protected the aluminium panel from melting and didn't have any holes on the
 223 specimens, as shown in **Figure 7(d)**. However, the maximum temperature observed on the
 224 unexposed side of specimen SP-C-A-D A (620 °C) during the fire exposure of 400 seconds
 225 was higher compared to the SP-C-A specimen applied only one side Coating-A (325 °C). Based
 226 on this test, it can be concluded that the melting issue of solid aluminium can be mitigated by
 227 applying Coating-A on both sides, but the flame spread is still a key issue when Coating-A is
 228 used.

229



(a) Time vs temperature curves

(b) Fire vs surface temperature curves

230 **Figure 6:** Fire behaviour of SP-C-A-D specimen with double sides Coating-A

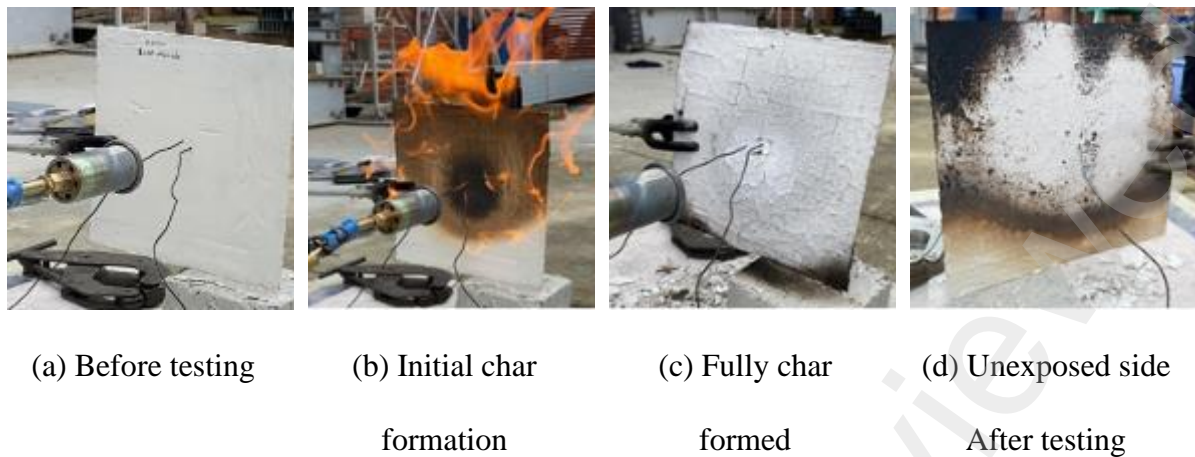
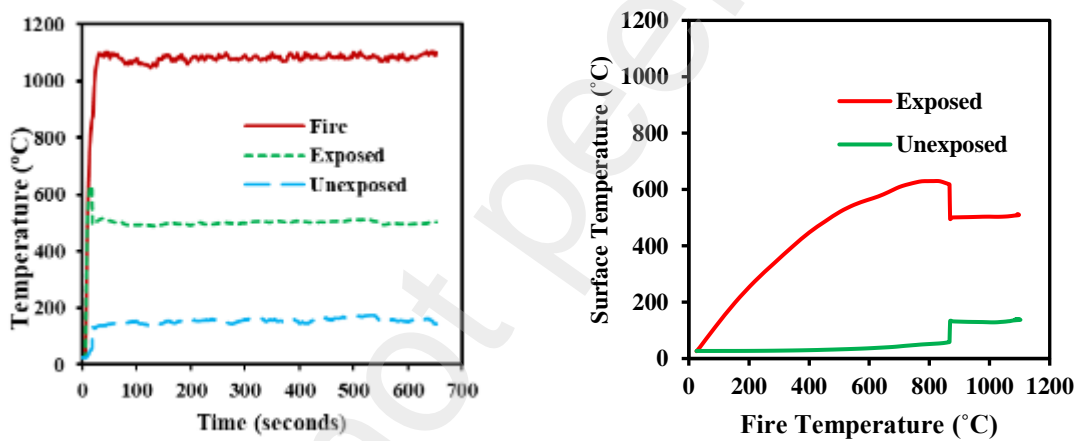


Figure 7: Photos of SP-C-A-D specimen during and after fire testing

3.3 Effect of Coating-B on the temperature profile

The effect of Coating-B on the temperature profile of a 0.5mm solid aluminium (SP-C-B specimen) is investigated, and the temperature-time curves of fire, exposed and unexposed sides of the SP-C-B specimen were measured as shown in **Figure 8(a)**. **Figure 8(b)** depicts the fire temperature vs both sides' surface temperature curves of the SP-C-B specimen. It can be seen from **Figure 8(a)** that the temperature at the exposed side initially suppressed the fire temperature until around 520°C due to chemical reactions that occurred during char formation, and the unexposed side of the SP-C-B specimen is observed to be lower compared to the fire temperature. Even the temperature of the exposed side linearly increased until around 627°C, and then the temperature dropped to around 500°C, as shown in **Figure 8(b)**. This temperature drops due to the intumescent Coating-B that undergoes a transformative reaction when exposed to fire, forming a thick, grey-blackish char, as shown in **Figure 9(b)**. In direct interaction with fire, the Coating-B reacts by forming a substantial char layer that offers effective fire protection. Analysis of the results reported in **Figure 8** reveals not only the char formed at the temperature around 630°C (as shown in **Figure 9(b)**) but also a distinct pattern: the temperature on the exposed side gradually increases until it reaches a peak, after which it stabilises around 490°C. Similarly, the unexposed side experiences a sudden spike followed by a consistent temperature of around 150°C, as shown in **Figure 8(b)**. The reason behind this behaviour is

250 the char formation process. As the char layer develops (as shown in **Figure 9(c)**), it acts as a
 251 fire barrier and heat-resistant barrier that mitigates heat transfer, which leads to a temperature
 252 drop on the exposed side. On the other hand, the unexposed side efficiently absorbs and
 253 disperses heat from the exposed side, which leads to the initial temperature. After the stable
 254 char formed, the temperature of the exposed and unexposed sides remained constant. Coating-
 255 B shows exceptional fire protection performance. **Figure 9(d)** shows the well-preserved
 256 condition of the aluminium after the test, and there is no melting issue when Coating-B is
 257 applied to one side of specimen SP-C-B. However, black particles are generated during the
 258 burning of chars of Coating-B, which move upward during the fire, which could create a fire
 259 hazard, and this hazard could be more significant if there is a strong wind.



(a) Time vs temperature curve (b) Fire vs surfaces temperature curve

260 **Figure 8:** Fire behaviour of SP-C-B specimen with oneside with Coating-B

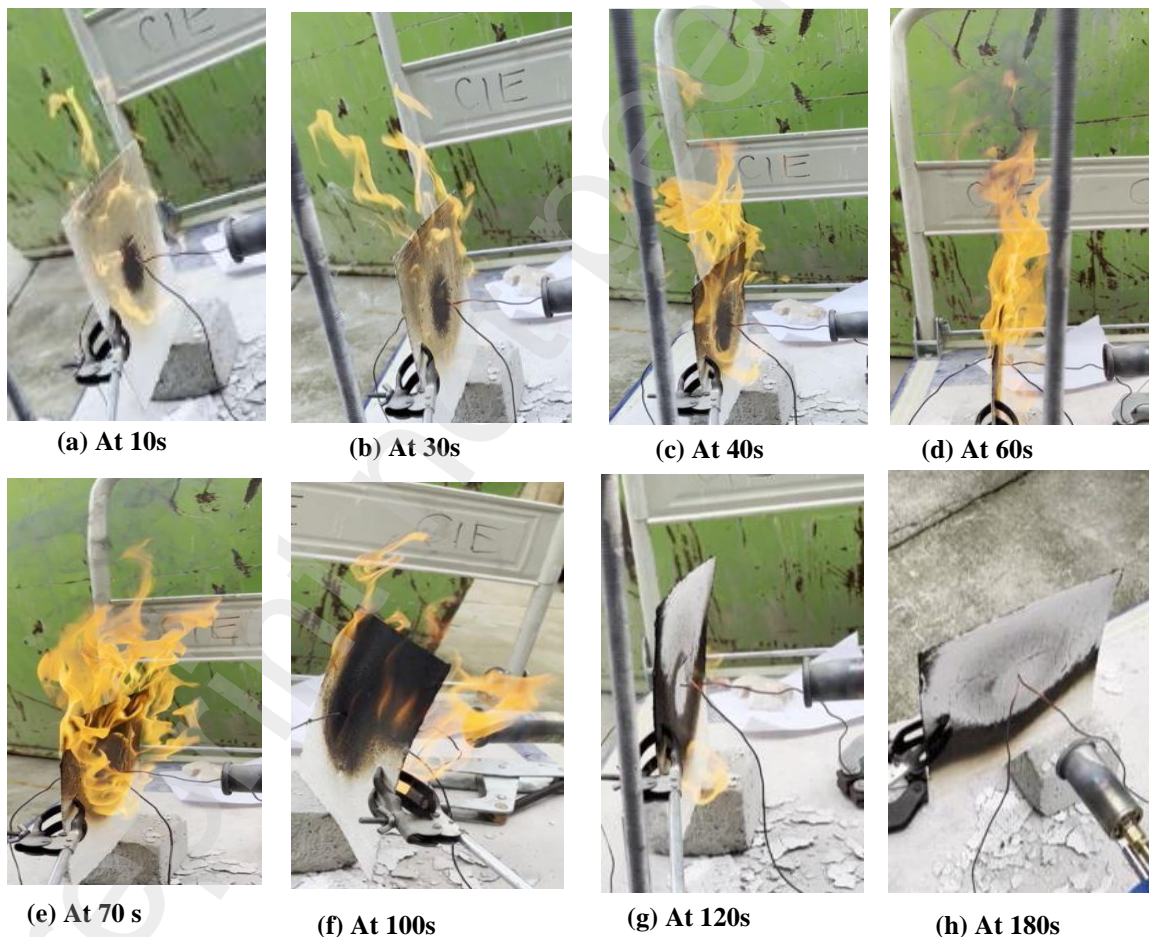


(a) Before testing (b) Initially char formation (c) Fully char formed (d) Unexposed side after testing

261 **Figure 9:** Photos of SP-C-B specimen during and after fire testing

262 3.4 Flame spread and char formation for Coating-A and Coating-B

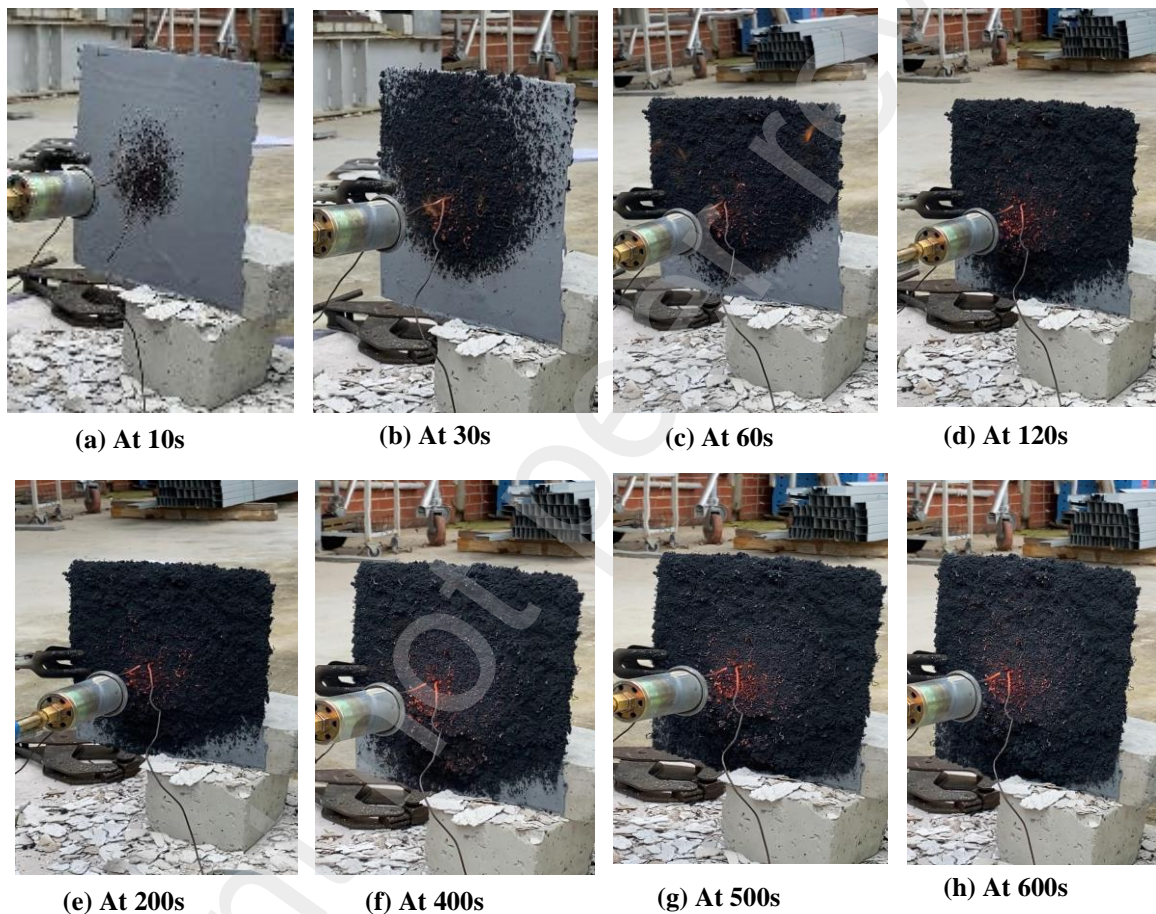
263 The fire spread and char formation with fire exposure time are illustrated in **Figure 10**
264 for Coating-A and in **Figure 11** for Coating-B. It can be seen from these two figures that the
265 fire spread and the char formation of both coatings are not the same. This could be due to the
266 different compositions used to prepare the coating in their formulation. In Coating-A, the fire
267 spread is observed significantly due to the presence of petroleum in Coating-A, which makes
268 it combustible. It can be seen from **Figure 10(a)** that Coating-A ignites within 10 seconds when
269 it is exposed to fire. The flame height increases significantly with time and until the burning of
270 the petroleum fuel (as shown in **Figure 10b-e**), and then the flame height (**Figure 10(f)**) is
271 reduced by forming the char after the fire exposure of 70 s.



272

273 **Figure 10:** Flame height and char formation stages of Coating-A at different time intervals.

274 The fire spread slows due to the depletion of the fuel source. Significant smoke is observed at
275 the peak flame stage (**Figure 10(d)**). This could be due to the presence of calcium carbonate,
276 which contributes to smoke production by releasing carbon dioxide when exposed to fire. After
277 100 s of fire exposure, the char layer is observed significantly (**Figure 10(g)**), and once a
278 complete char layer forms (**Figure 10(h)**), the fire ceases to spread and gives the fire protection
279 to the substrate. The char thickness for Coating-A was nearly similar to the coating thickness.



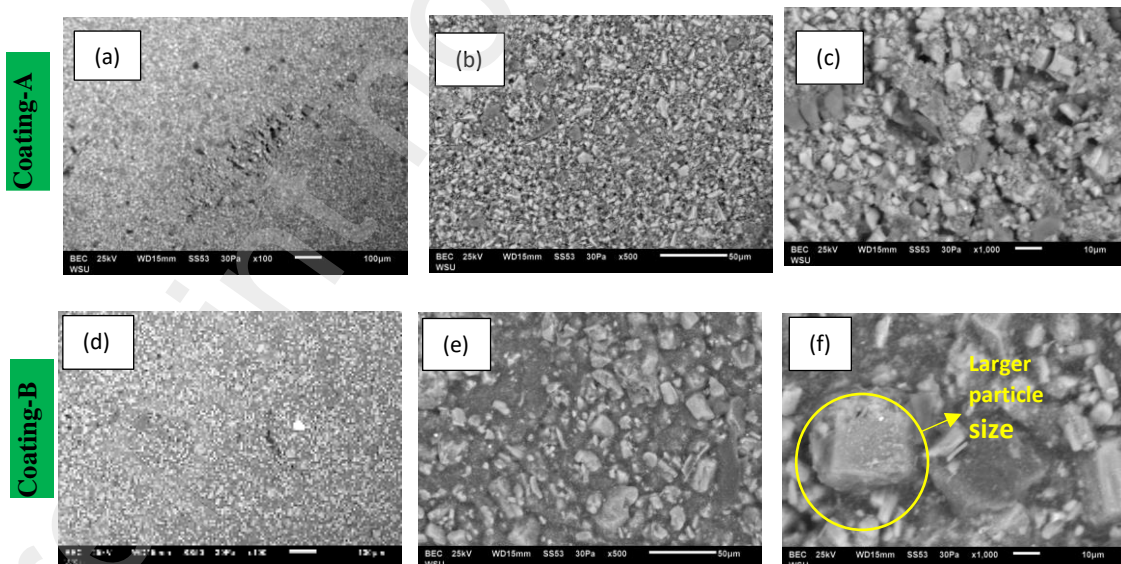
280 **Figure 11:** Photos of fire testing of Coating-B at different time intervals.

281 There is no flame spread in Coating-B when exposed to the fire. The char formation of
282 Coating-B is not similar to Coating-A. **Figure 11** shows the various stages of char formation
283 of Coating-B. When the Coating-B is exposed to the fire, the char formation starts initially, as
284 shown in **Figure 11(a-b)**. At the early stage of fire exposure (10 s), the key materials undergo
285 chemical reactions and form a limited char layer, as shown in **Figure 11(a)**. Over time of fire

286 exposure, the char formation is observed significantly, and the char layer fully develops,
287 effectively protecting the underlying substrate from further damage, as shown in **Figure 11(c-**
288 **h)**. During the char formation, the expandable graphite used in Coating-B expands, traps gases
289 formed by chemical reactions, and forms a protective char layer. The maximum char thickness
290 for Coating-B was 21 mm.

291 3.5 Microstructure analysis for Coating-A and Coating-B

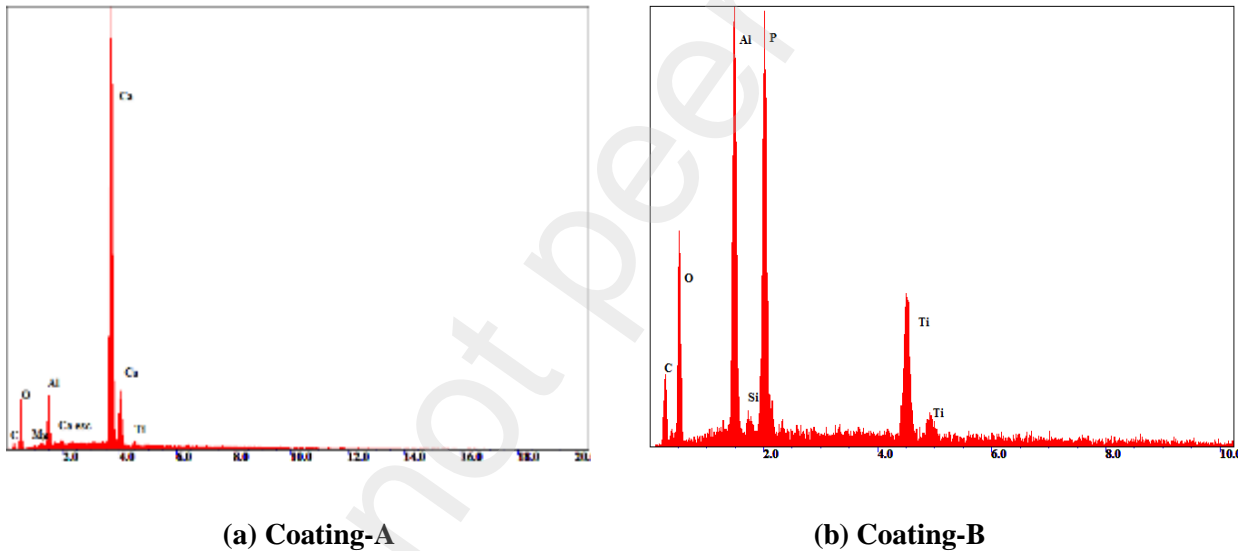
292 The microstructure of Coating-A and B before the fire testing was analysed by scanning
293 electron microscopy-SEM (model JEOL 6510LV) with EDS detector, as shown in **Figure 12**.
294 The microstructure image of Coating-A at magnifications of 100 μm , 50 μm , and 10 μm is
295 illustrated in **Figures 12(a-c)**. Similarly, pictures of Coating-B at the same magnifications are
296 shown in **Figures 12(d-f)**. Comparing Coating-A to Coating-B, Coating-A shows a more
297 consistent and even structure. It is clear that Coating-B has much larger particles **Figure 12(f)**
298 than Coating-A **Figure 12(c)**, which is caused by the increased filler concentration in Coating-
299 B. Coating-B's particle size is greater because of the increased filler content. Coating-A offers
300 a smoother surface and a superior external finish on an aluminium sheet.



301
302

303 **Figure 12:** SEM analysis of Coating-A & Coating-B. a, b and c are the 100, 50 and 10 μm
304 images of Coating-A and d, e and f are the 100 μm , 50 μm and 10 μm images of Coating-B.

305 **Figure 13** shows the EDS spectrum results of Coating-A and Coating-B. The EDS
306 spectrum indicates that the sample of Coating-A primarily consists of calcium (Ca) with
307 significant peaks. Additionally, other peaks are observed, including carbon (C), oxygen (O),
308 magnesium (Mg), Aluminium (Al), and titanium (Ti). The high calcium peak proves that
309 Coating-A is rich with calcium compounds. The Ca escape peak is an analysis artifact. For
310 Coating-B, the EDS spectrum (**Figure 13**) shows that Coating-B has a significant amount of
311 Aluminium (Al) and phosphorus (P). Furthermore, C, O, Si, and Ti elements are also found in
312 the Coating-B. The EDS spectrum of Coating-B is noisier than Coating-A, which proves that
313 Coating-B has more compounds in it.



316 **Figure 13:** EDS analysis of Coating-A and Coating-B.

317 After fire testing for both coatings, the morphology of the internal char structure of
318 Coatings A and B was investigated under SEM with an EDS detector. The microstructures of
319 chars of Coating-A are shown in **Figures 14(a-c)** at magnifications of 100 μm (250 \times), 50 μm
320 (450 \times), and 10 μm (1400 \times). Similarly, the chars of Coating-B at the same magnifications are
321 shown in **Figures 14(d-f)**. It can be seen that the char of Coating-A exhibits a powdery and
322 solid char morphology. Additionally, it shows a cementitious structure with a higher prevalence
323 of cracks compared to the char of Coating-B. In contrast, the char of the Coating-B exhibits a

324 foam-like and fluffy morphology with a loose structure. This indicates that the gases released
325 during combustion were not confined within the polymer matrix. Additionally, Coating-B has
326 a porous char structure and is well distributed, which helps to transfer the heat from the fire-
327 exposed side to the unexposed side.

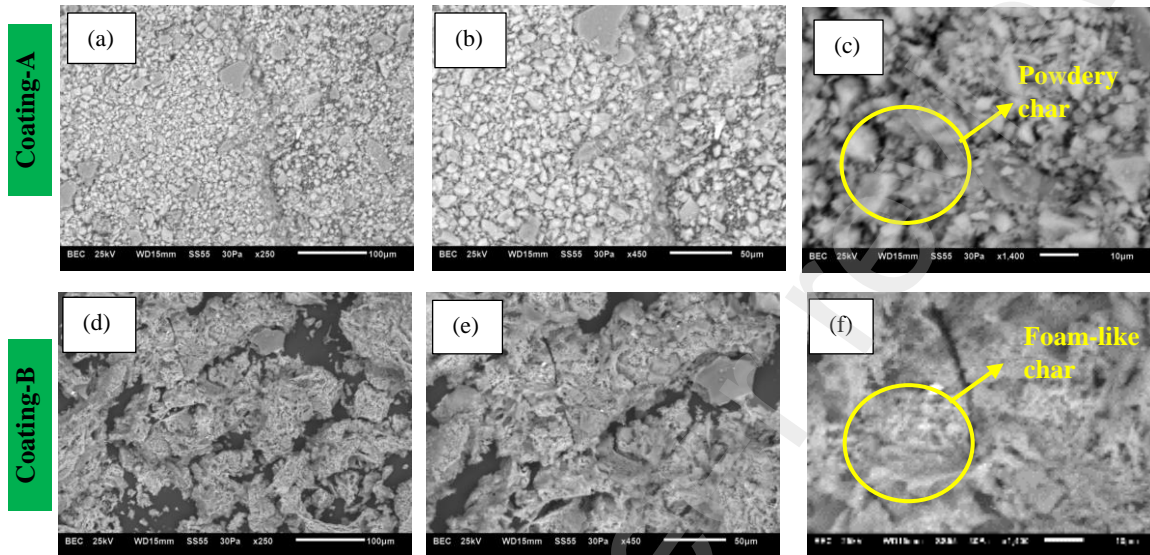
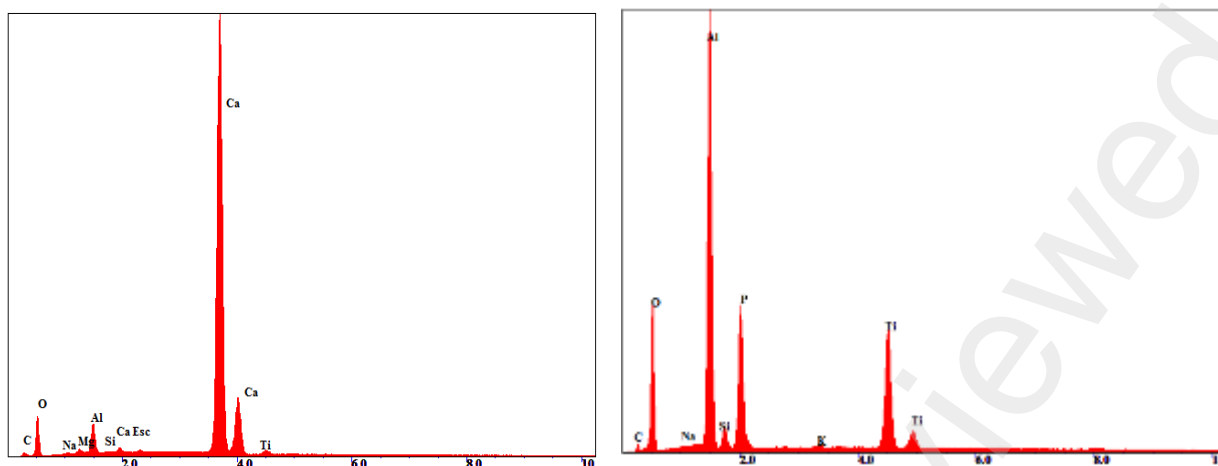


Figure 14: SEM analysis of the char of Coating-A and Coating-B. a, b and c are the 100 μm , 50 μm and 10 μm images of Coating-A and d, e and f are the 100 μm , 50 μm and 10 μm images of Coating-B.

328 **Figure 15** shows the EDS spectrum of char of Coatings-A and Coating-B. The EDS
329 spectrum indicates that the char sample of Coating-A primarily consists of Ca, with significant
330 peaks. Further peaks such as C, O, Mg, Al, Na, and Ti can also be seen in the char of Coating-
331 A. The high calcium peak proves that the char of Coating-A is also rich with calcium
332 compounds. The compositions of Coating-A and its char are similar (**Figure 13(a)** and **Figure**
333 **15(a)**). For Coating-B, the EDS spectrum (**Figure 15(b)**) shows that the char of Coating-B has
334 a significant amount of Aluminium (Al). However, the phosphorus (P) has a significant peak
335 in the coating form than the char form (**Figure 13(b)** and **Figure 15(b)**). Furthermore, C, O,
336 Si, and Ti elements are also found in the char of Coating-B.



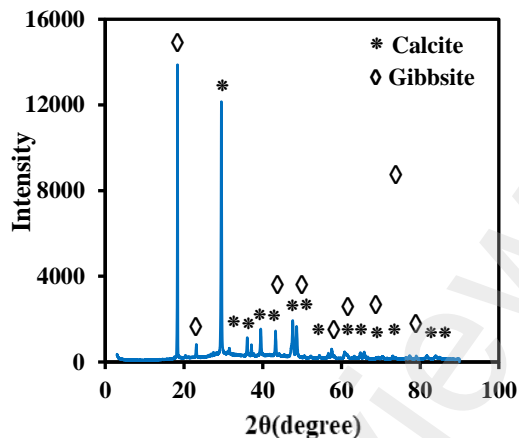
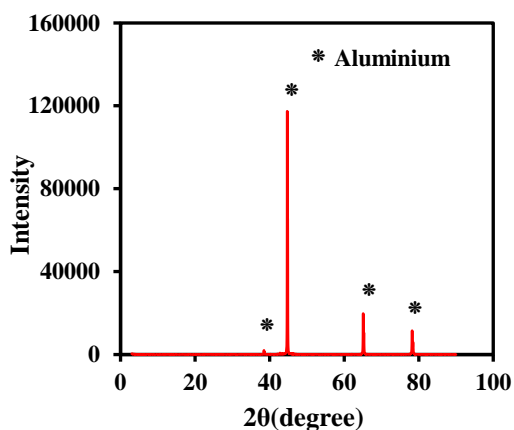
(a) Char of Coating-A

(b) Char of Coating-B

Figure 15: EDS analysis of char of Coating-A and Coating-B.

3.6 Elementary analysis and chemical reaction studies

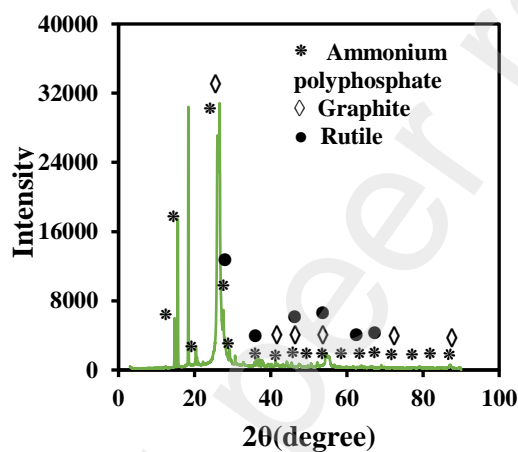
An elementary analysis using XRD for Coating-A and Coating-B samples before and after fire testing is conducted to understand the chemical reaction in the coating. **Figure 16(a-c)** shows the XRD patterns of the solid aluminium panel, Coating-A and Coating-B samples. Similarly, **Figure 16(d-c)** shows the XRD patterns of the char of Coatings-A and Coating-B. The XRD patterns reveal key insights into sample composition and properties. **Figure 16(a)** shows that the characteristic peaks indicate the crystalline structure of aluminium (powder diffraction file (PDF) 04-024-6814), indicating that the solid aluminium panel used in this experiment was made of pure aluminium. In **Figure 16(b)**, it is observed that Coating-A have calcite (CaCO_3) (PDF 01-086-4274) and gibbsite ($\text{Al}(\text{OH})_3$) (PDF 00-007-0324) as the main ingredients. These materials have excellent thermal stability and mechanical strength. Under heating conditions, gibbsite decomposes into alumina (Al_2O_3) and water (H_2O), where water helps to cool down the surface temperature of the coating, and alumina has high heat resistance properties. Additionally, calcite (CaCO_3) breaks down into calcium oxide (CaO) and carbon dioxide (CO_2) when exposed to fire or heat [34], enhancing the coating's thermal resistance.



356

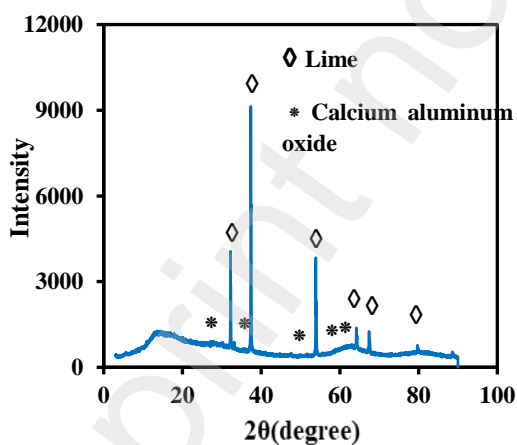
357 (a) XRD analysis of Aluminium sheet

(b) XRD analysis of Coating-A

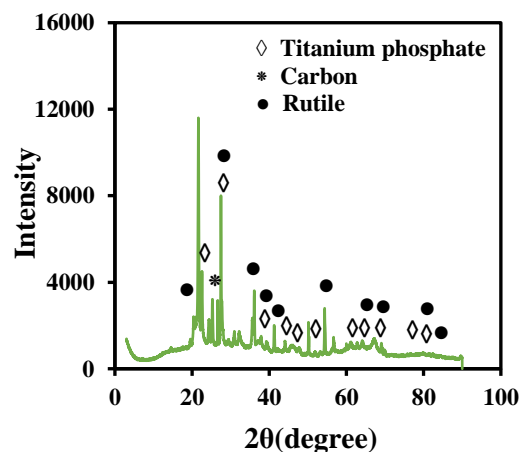


358

(c) XRD analysis of Coating-B.



359 (d) XRD analysis of Char of Coating-A



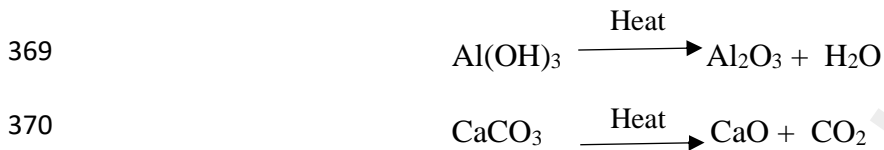
(e) XRD analysis of Char of Coating-B

360 **Figure 16:** XRD analysis of solid aluminium sheet, Coating-A and B before fire test and char

361 of Coating-A and Coating-B after fire test.

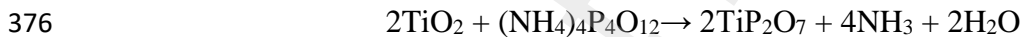
362 In the **Figure 16(d)**, it is observed that the char of Coating A has lime (CaO) (PDF 01-
363 082-1690), and calcium aluminium oxide (CaAl₂O₄) (PDF 00-062-0852). Calcium oxide and
364 aluminium oxide react at high temperatures and produce calcium aluminium oxide. Calcium
365 aluminium oxide is a widely used cement that is used in high-performance applications
366 requiring resistance to chemical attack, high early strength, refractory properties, and abrasion
367 resistance [35].

368



371

372 **Figure 16(c)** shows that Coating-B sample contains ammonium polyphosphate
373 ((NH₄)PO₃) (PDF 00-069-0862), graphite (C) (PDF 00-056-0159), and rutile (TiO₂) (PDF 01-
374 078-4190). These compounds react together and form chars that give fire protection to the
375 aluminium sheet.



377

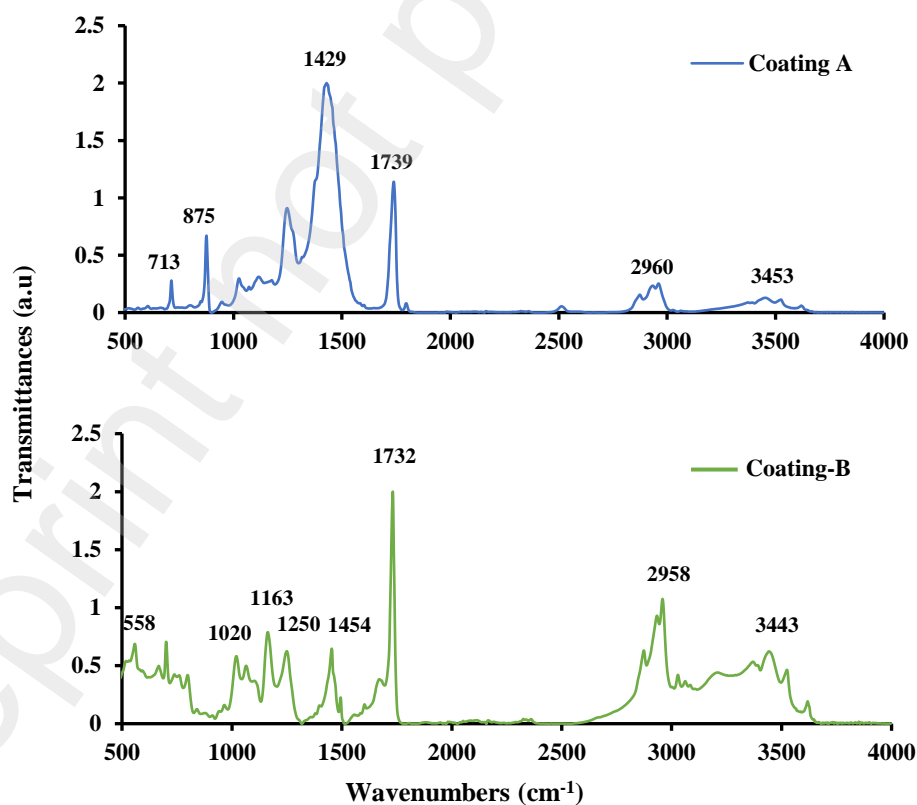
378 Additionally, the interaction between ammonium polyphosphate and titanium dioxide
379 in the fire results in the formation of titanium pyrophosphate (TiP₂O₇), which enhances fire
380 protection capabilities by increasing thermal stability and radiative heat transfer [36]. **Figure**
381 **16(e)** proves that the char of Coating-B has titanium pyrophosphate (TiP₂O₇) (PDF 00-052-
382 1470). Additionally, it is also observed that the char of Coating-B has Carbon (C) (PDF 01-
383 086-7889) and rutile (TiO₂) (PDF 01-089-8302). This increases residue at higher temperatures,
384 increasing the fire performance.

384 3.7 FTIR analysis

385 **Figure 17** shows the FTIR spectrum of the internal coating sample of A and B. The
386 two samples have different peaks. For Coating-A, the band at 713 cm⁻¹ due to stretching

387 vibration, 875 cm^{-1} due to bending vibration and 1429 cm^{-1} due to bending vibration are for C-
388 O bond. C-O bond here for calcium carbonate [37-39]. Additionally, the band at 3453 cm^{-1} is
389 for O-H stretching vibrations [40, 41]. There is a strong peak at 1739 cm^{-1} , due to C=O
390 stretching vibration of carbonyl group [42]. This proves that Coating-A contains a carbonyl
391 group (C=O). The band is 2960 cm^{-1} due to C-H stretching vibrations [43, 44]. In the case of
392 Coating-B, the region $1400\text{-}800\text{ cm}^{-1}$ showed the presence of phosphate (P-O-P) and 1020 cm^{-1}
393 $^{-1}$, 1163 cm^{-1} , and 1250 cm^{-1} confirmed the existence of phosphate PO_4^- due to the presence of
394 APP in the coating formulation [45]. There is a strong peak at 1732 cm^{-1} due to the carbonyl
395 group (C=O) [36]. The peak at 1454 cm^{-1} and 2958 cm^{-1} in Coating-B represents the stretching
396 vibration of CH_2 or CH_3 distortion in vibration due to polyaromatic compounds [46].
397 Additionally, one bending peak at 3443 cm^{-1} represents the stretching vibrations of $-\text{NH}_2$ bonds
398 [47, 48]. The peak at 558 cm^{-1} represents C-C=O in-plane vibration mode [49].

399



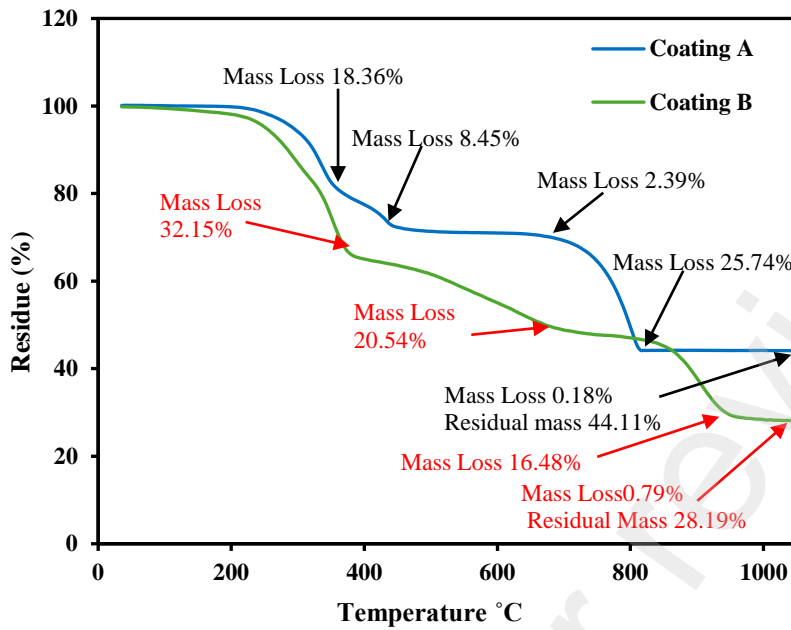
400

401

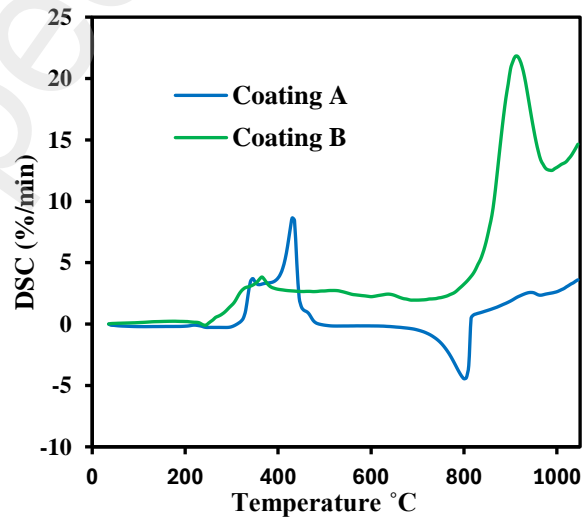
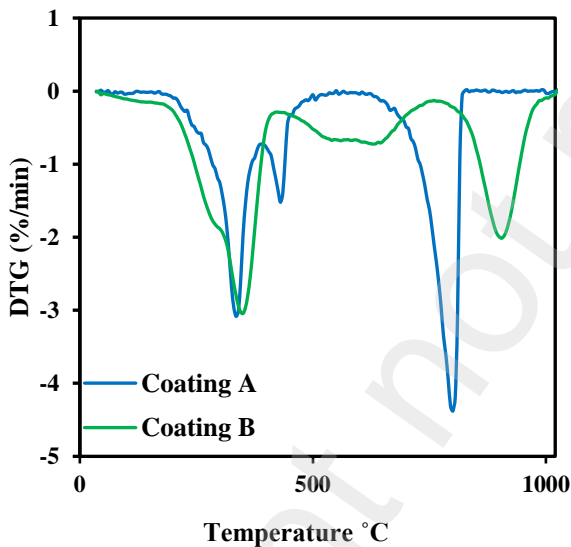
Figure 17: FTIR analysis of Coating-A and Coating-B

402 3.8 Thermal degradation analysis

403 The thermal degradation of Coating-A and Coating-B and the amount of char residue
404 at high temperatures were examined by TGA to understand the fire behaviour of coating
405 applied on solid aluminium. **Figure 18 (a-b)** shows the TGA and DTG curves of Coating-A
406 and B. The DTG analysis shows that Coating-A has three major degradation steps. At around
407 230-360 °C temperature, a noticeable drop in mass was 18.36%. In the second stage, around
408 360-450 °C temperature, an additional 8.45% mass loss occurred. Thermal decomposition or
409 volatilisation of coating components is the reason behind it. The residual mass remains
410 relatively stable around 450-680 °C, and mass loss was only 2.39%; no significant
411 decomposition has been noticed during this temperature range. A significant mass drop of
412 25.74% occurred around 680-816 °C, indicating another decomposition or volatilisation of
413 coating components. Beyond 820 °C temperature, the curve stabilises, proving the remaining
414 materials are thermally stable up to 1048.2 °C. At 1048.2 °C temperature, the residual mass of
415 Coating-A is 44.11% of its original mass. On the other hand, Coating-B has three degradation
416 steps. In the first stage, at the temperature range of 200-380 °C, 32.15% of weight loss occurred
417 due to the thermal decomposition of coating materials. During the second stage, 380-850 °C, a
418 more gradual mass loss occurred, proving the continuous decomposition of coating materials
419 and around 20.54% mass loss. A rapid decomposition occurred from 850-950 °C, and 16% of
420 mass loss occurred. Beyond 850 °C temperature, the mass continues to decrease gradually and
421 at the 1048.1 °C, 28.19% of its original mass remains (**Figure 18(a)**). It can be seen from **Figure**
422 **18** that the mass loss of Coating-B is higher than that of Coating-A, and the residual mass of
423 Coating-B is less than that of Coating-A. The reason behind this is that the char volume of
424 Coating-B is much higher than that of Coating-A. For this reason, the fire protection of
425 Coating-B is better than Coating-A, which is also observed during the fire tests discussed in
426 section 3.1 to 3.4.



428 (a) TGA curves of Coating-A and Coating-B



429 (b) DTG curves of Coating-A and Coating-B (c) DSC curves of Coating-A and Coating-B

430 **Figure 18:** Thermogravimetric Analysis (TGA) of Coating-A and Coating-B

431 It can be seen from **Figure 18(c)** that the DSC curve for Coating-A shows a broad exothermic
 432 peak around 300°C to 500°C, followed by a smaller endothermic peak around 750°C to 830°C.

433 Decomposition of the Coating-A is the possible reason behind the exothermic peak at 300°C

434 to 500°C. This reaction is exothermic. Aluminium hydroxide is an endothermic reaction and

435 can lose water molecules (dehydrate) around 200-300°C. However, the temperature range in

436 the curve suggests this might be a minor contribution to the overall peak. Calcium carbonate is
437 another component of Coating-A that decomposes around 898°C and is an endothermic
438 reaction that absorbs heat. **Figure 18(c)** shows that the second peak is around 750°C to 830°C,
439 possibly due to the decomposition of calcium carbonate. Coating-B has a more complicated
440 formulation and more fillers. **Figure 18(c)** shows that Coating-B has two exothermic peaks
441 around 250°C to 400 °C and 800°C to 1000°C. The reason behind the exothermic reactions is
442 the decomposition of coating material and the formation of char. Coating-B doesn't absorb heat
443 and produces heat through an exothermic reaction.

444 **4. CONCLUSION**

445 This research study investigates the effectiveness of coating on the outer skin of
446 aluminium composite panels (ACP). In this study, the outer skin, i.e., 0.5mm solid aluminium
447 with and without coating, is tested using a butane torch as the fire source. This study uses two
448 types of coatings (Coating-A and B). Both coatings are non-toxic and water-based intumescent
449 coatings. Based on the scope of this research study, the following conclusions can be drawn:

- 450 • Pure solid aluminium used as the outer layer in ACP can create a fire hazard when
451 exposed to high temperatures (>660°C). When the fire temperature on the exposed side
452 of solid aluminium exceeds more than 660°C, it starts to melt and form a hole on the
453 centre of the specimen.
- 454 • Intumescent coating could effectively mitigate the melting issue of solid aluminium
455 used as the outer layer in ACP. However, a careful selection of intumescent coating is
456 very important as the fire behaviour of all coating is not the same.
- 457 • The melting issue of solid aluminium can be mitigated by applying Coating-A on both
458 sides instead of a single side, but the flame spread is still a key issue when Coating-A
459 is used.

460 • Coating-B shows exceptional fire protection performance compared to Coating-A. No
461 melting and flame spread issues are observed for Coating-B, although it is applied on
462 one side of specimen SP-C-B. Coating-B exhibits excellent adhesive characteristics on
463 the solid aluminium, maintaining its char integrity even after the fire was extinguished.
464 However, black char particles generated during the burning of chars of Coating-B could
465 create a fire hazard. They can become airborne and pose a hazard to the eyes and
466 respiratory system. Further research can be conducted to mitigate this black char
467 particles generated during the burning of chars of intumescent coating.

468

469 **ACKNOWLEDGEMENT**

470 The first author gratefully acknowledges the Research Assistantship and material supports
471 provided by Western Sydney University during MPhil study. The authors would also like to
472 express their sincere gratitude to the Advanced Materials Characterisation Facility (AMCF)
473 and the Structural Testing Laboratory at Western Sydney University for providing essential
474 resources and support in conducting the material characterization and fire testing.

475

476

477

478

479

480

481

482

483

484

485 Reference

- 486 1. Hossain, M.D., et al., *Flame behaviour, fire hazard and fire testing approach for*
487 *lightweight composite claddings—a review*. Journal of structural fire engineering, 2021.
488 **12**(3): p. 257-292.
- 489 2. Hossain, M.D., et al., *Testing of aluminium composite panels in a cone calorimeter: A*
490 *new specimen preparation method*. Polymer Testing, 2022. **106**: p. 107454.
- 491 3. Hassan, M.K., et al., *Numerical investigations on the influencing factors of rapid fire*
492 *spread of flammable cladding in a high-rise building*. Fire, 2022. **5**(5): p. 149.
- 493 4. Mazzucchelli, E., P. Rigone, and B. De la Fuente Ceja, *Fire Safety Facade Design: The*
494 *case study of an office tower in Milan*, in *Face Time 2020: Better Buildings through*
495 *Better Skins*. 2020, Tectonic Press. p. 209-223.
- 496 5. Yuen, A.C.Y., et al., *Evaluating the fire risk associated with cladding panels: An*
497 *overview of fire incidents, policies, and future perspective in fire standards*. Fire and
498 materials, 2021. **45**(5): p. 663-689.
- 499 6. Wi, S., et al., *Assessment of recycled ceramic-based inorganic insulation for improving*
500 *energy efficiency and flame retardancy of buildings*. Environment international, 2019.
501 **130**: p. 104900.
- 502 7. Guillaume, E., et al., *Study of fire behaviour of facade mock-ups equipped with*
503 *aluminium composite material-based claddings, using intermediate-scale test method*.
504 Fire and Materials, 2018. **42**(5): p. 561-577.
- 505 8. Hossain, M.D., et al., *Fire behaviour of insulation panels commonly used in high-rise*
506 *buildings*. Fire, 2022. **5**(3): p. 81.
- 507 9. Chen, T.B.Y., et al., *Fire risk assessment of combustible exterior cladding using a*
508 *collective numerical database*. Fire, 2019. **2**(1): p. 11.
- 509 10. Mróz, K., I. Hager, and K. Korniejenko, *Material solutions for passive fire protection*
510 *of buildings and structures and their performances testing*. Procedia Engineering, 2016.
511 **151**: p. 284-291.
- 512 11. Suryoputro, M.R., et al. *Active and passive fire protection system in academic building*
513 *KH. Mas Mansur, Islamic University of Indonesia*. in *MATEC Web of Conferences*.
514 2018. EDP Sciences.
- 515 12. Landucci, G., et al., *Design and testing of innovative materials for passive fire*
516 *protection*. Fire Safety Journal, 2009. **44**(8): p. 1103-1109.

- 517 13. Efthymiou, E., Ö.N. Cöcen, and S.R. Ermolli, *Sustainable aluminium systems*.
518 Sustainability, 2010. **2**(9): p. 3100-3109.
- 519 14. Miller, W., et al., *Recent development in aluminium alloys for the automotive industry*.
520 Materials Science and Engineering: A, 2000. **280**(1): p. 37-49.
- 521 15. Leitner, M., et al., *Thermophysical properties of liquid aluminum*. Metallurgical and
522 Materials Transactions A, 2017. **48**: p. 3036-3045.
- 523 16. Khan, A.A., et al., *Facade fire hazards of bench-scale aluminum composite panel with*
524 *flame-retardant core*. Fire Technology, 2021: p. 1-24.
- 525 17. Maguire, J.F. and L.V. Woodcock, *Thermodynamics of tower-block infernos: effects of*
526 *water on aluminum fires*. Entropy, 2019. **22**(1): p. 14.
- 527 18. Almarzooqi, A., A. Alzubaidi, and S. Alkathheeri. *Fire hazards by aluminum composite*
528 *cladding in high-rise buildings*. in *Proceedings of the 5th European International*
529 *Conference on Industrial Engineering and Operations Management, Rome, Italy*. 2022.
- 530 19. Gandhi, P., et al., *Performance of glass-ACP façade system in a full-scale real fire test*
531 *in a G+ 2 structure*. Procedia engineering, 2017. **210**: p. 512-519.
- 532 20. Li, K., et al., *Improving the fire performance of structural insulated panel core*
533 *materials with intumescent flame-retardant epoxy resin adhesive*. Fire Technology,
534 2023. **59**(1): p. 29-51.
- 535 21. *ALPOLIC™ NC / ALPOLIC™ AI, Non-Combustible Cladding prepared by ExcelPlas*.
536 2021 [cited 2024 19/09/2024]; Available from:
537 [https://www.claddingsystems.com.au/20/wp-content/uploads/2022/03/ALPOLIC-NC-](https://www.claddingsystems.com.au/20/wp-content/uploads/2022/03/ALPOLIC-NC-White-Paper-Sept-2021.pdf)
538 [White-Paper-Sept-2021.pdf](https://www.claddingsystems.com.au/20/wp-content/uploads/2022/03/ALPOLIC-NC-White-Paper-Sept-2021.pdf).
- 539 22. Kwang Yin, J.J., et al., *Preparation of intumescent fire protective coating for fire rated*
540 *timber door*. Coatings, 2019. **9**(11): p. 738.
- 541 23. de Silva, D., A. Bilotta, and E. Nigro, *Experimental investigation on steel elements*
542 *protected with intumescent coating*. Construction and Building Materials, 2019. **205**: p.
543 232-244.
- 544 24. Lim, K.-S., et al., *A review of application of ammonium polyphosphate as intumescent*
545 *flame retardant in thermoplastic composites*. Composites Part B: Engineering, 2016.
546 **84**: p. 155-174.
- 547 25. Baena, J.C., et al., *Fire behaviour of waterborne intumescent coatings on timber*
548 *substrate for bushfire exposure*. Fire Safety Journal, 2023. **140**: p. 103836.
- 549 26. Beh, J.H., et al., *Fire protection performance and thermal behavior of thin film*
550 *intumescent coating*. Coatings, 2019. **9**(8): p. 483.

- 551 27. Hussain, A., et al., *Fire performance of intumescent waterborne coatings with*
552 *encapsulated APP for wood constructions*. Coatings, 2021. **11**(11): p. 1272.
- 553 28. Canosa, G., P.V. Alfieri, and C.A. Giudice, *Hybrid intumescent coatings for wood*
554 *protection against fire action*. Industrial & engineering chemistry research, 2011.
555 **50**(21): p. 11897-11905.
- 556 29. Lucherini, A., Q.S. Razzaque, and C. Maluk, *Exploring the fire behaviour of thin*
557 *intumescent coatings used on timber*. Fire Safety Journal, 2019. **109**: p. 102887.
- 558 30. Ghiji, M., P. Joseph, and M. Guerrieri, *Some recent developments and testing strategies*
559 *relating to the passive fire protection of concrete using intumescent coatings: a review*.
560 Journal of Structural Fire Engineering, 2023. **14**(1): p. 61-89.
- 561 31. Li, F.-F., *Comprehensive Review of Recent Research Advances on Flame-Retardant*
562 *Coatings for Building Materials: Chemical Ingredients, Micromorphology, and*
563 *Processing Techniques*. Molecules, 2023. **28**(4): p. 1842.
- 564 32. Nazaré, S., et al., *Factors for consideration in an open-flame test for assessing fire*
565 *blocking performance of barrier fabrics*. Polymers, 2016. **8**(9): p. 342.
- 566 33. Nurdiansyah, H. and F. Ridha, *Aluminum combustion under different condition: a*
567 *review*. Journal of Energy, Mechanical, Material, and Manufacturing Engineering,
568 2020. **5**(2): p. 1-8.
- 569 34. Khine, E.E., et al., *Synthesis and characterization of calcium oxide nanoparticles for*
570 *CO₂ capture*. Journal of Nanoparticle Research, 2022. **24**(7): p. 139.
- 571 35. Ukrainczyk, N. and T. Matusinović, *Thermal properties of hydrating calcium*
572 *aluminate cement pastes*. Cement and concrete research, 2010. **40**(1): p. 128-136.
- 573 36. Puri, R.G. and A. Khanna, *Effect of cenospheres on the char formation and fire*
574 *protective performance of water-based intumescent coatings on structural steel*.
575 Progress in Organic Coatings, 2016. **92**: p. 8-15.
- 576 37. Vagenas, N.V., A. Gatsouli, and C.G. Kontoyannis, *Quantitative analysis of synthetic*
577 *calcium carbonate polymorphs using FT-IR spectroscopy*. Talanta, 2003. **59**(4): p. 831-
578 836.
- 579 38. Reig, F.B., J.G. Adelantado, and M.M. Moreno, *FTIR quantitative analysis of calcium*
580 *carbonate (calcite) and silica (quartz) mixtures using the constant ratio method.*
581 *Application to geological samples*. Talanta, 2002. **58**(4): p. 811-821.
- 582 39. Chakrabarty, D. and S. Mahapatra, *Aragonite crystals with unconventional*
583 *morphologies*. Journal of materials chemistry, 1999. **9**(11): p. 2953-2957.

- 584 40. Culka, A., J. Jehlička, and I. Němec, *Raman and infrared spectroscopic study of*
585 *boussingaultite and nickelboussingaultite*. *Spectrochimica Acta Part A: Molecular and*
586 *Biomolecular Spectroscopy*, 2009. **73**(3): p. 420-423.
- 587 41. Balan, E., et al., *First-principles study of the OH-stretching modes of gibbsite*.
588 *American Mineralogist*, 2006. **91**(1): p. 115-119.
- 589 42. Popescu, C.-M., M.-C. Popescu, and C. Vasile, *Structural analysis of photodegraded*
590 *lime wood by means of FT-IR and 2D IR correlation spectroscopy*. *International journal*
591 *of biological macromolecules*, 2011. **48**(4): p. 667-675.
- 592 43. Synytsya, A., et al., *Fourier transform Raman and infrared spectroscopy of pectins*.
593 *Carbohydrate polymers*, 2003. **54**(1): p. 97-106.
- 594 44. Saikia, B.J., G. Parthasarathy, and N. Sarmah, *Fourier transform infrared*
595 *spectroscopic characterization of Dergaon H5 chondrite: Evidence of aliphatic*
596 *organic compound*. *Nature and Science*, 2009. **7**(4): p. 45-51.
- 597 45. Ullah, S., et al., *Effect of expandable graphite and ammonium polyphosphate on the*
598 *thermal degradation and weathering of intumescent fire-retardant coating*. *Journal of*
599 *Applied Polymer Science*, 2021. **138**(17): p. 50310.
- 600 46. Cai, Y., J. Lv, and J. Feng, *Spectral characterization of four kinds of biodegradable*
601 *plastics: poly (lactic acid), poly (butylenes adipate-co-terephthalate), poly*
602 *(hydroxybutyrate-co-hydroxyvalerate) and poly (butylenes succinate) with FTIR and*
603 *Raman spectroscopy*. *Journal of Polymers and the Environment*, 2013. **21**: p. 108-114.
- 604 47. Mishra, S., et al., *Vibrational spectroscopic signatures of hydrogen bond induced NH*
605 *stretch–bend Fermi-resonance in amines: The methylamine clusters and other N–H…*
606 *N hydrogen-bonded complexes*. *The Journal of Chemical Physics*, 2020. **153**(19).
- 607 48. Işık, G., et al., *Determination of doxorubicin amount conjugated to mPEG-b-PCL*
608 *copolymer via pH sensitive hydrazone bond*. *Turkish Bulletin of Hygiene &*
609 *Experimental Biology/Türk Hijyen ve Deneysel Biyoloji*, 2022. **79**(2).
- 610 49. Pandiarajan, S., et al., *FT-IR and FT-Raman spectral studies of bis (L-proline)*
611 *hydrogen nitrate and bis (L-proline) hydrogen perchlorate*. *Journal of Raman*
612 *Spectroscopy: An International Journal for Original Work in all Aspects of Raman*
613 *Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh*
614 *Scattering*, 2005. **36**(10): p. 950-961.
- 615