# Effect of Boric Acid and Melamine on the Intumescent Fire-Retardant Coating Composition for the Fire Protection of Structural Steel Substrates

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**ABSTRACT:** Intumescent coating is an insulating material designed to decrease heat transfer to a substrate structure. The coating presented in this research article was based on expandable graphite, ammonium polyphosphate, melamine, and boric acid. Bisphenol A epoxy resin BE-188 was used as a binder with ACR hardener H-2310 polyamide amine. Different formulations were developed to study the effect of expansion and heat shielding after fire testing. The coating was tested at 950°C for 1 h. The results show that the coating was stable and well bonded with the substrate. The coating was characterized with thermogravimetric analysis (TGA, Parkin Elmer, Norwalk, CT, 06859, USA), Fourier transform infrared (FTIR, Nicolet 400 D Shimadzu spectrometer) spectroscopy, X-ray diffraction (XRD, Bruker D8 advance Diffracto meter, Bruker Germany), and scanning electron microscopy (SEM, Carl Zeiss Leo 1430VP, UK). The morphology of char was studied by SEM on the coating after fire testing. XRD and FTIR spectroscopy showed the presence of graphite, boron phosphate, boron oxide, and sassolite in the residual char. TGA (Pyris 1, manufactured by Parkin Elmer, Norwalk, CT, 06859, USA) and differential thermal gravimetric analysis (DTGA) showed that boric acid enhanced the residual weight of the intumescent fire-retardant coating. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

## INTRODUCTION

The devastating effects of fire result in disasters that cause the loss of lives and property. The risk of fires to humans and their assets has opened a new area of technological development. Since the last decade, scientists have been working to develop new materials and new methods to protect humans and their assets from the destructive effects of fire. Multiple risk–benefit analyses carried out over the last decade have shown that flame-retardant materials have helped to reduce the amount of severe damage and the number of deaths caused by fires in megabuildings and offshore oil and gas facilities.[1]

Previous studies have shown that steel structures can sustain their strength below or up to a maximum temperature of 500°C; they will lose their structural properties at higher temperatures. The failure of the load-bearing members of steel structures eventually results in the disintegration of a building. As the building starts to collapse, utility pipelines, such as gas pipelines, can be ruptured. This can lead to an explosion due to the presence of hydrocarbons and natural gas in the building. Therefore, to ensure the safety of steel structures, it is necessary to keep the temperature of steel structures below 500°C during fire incidents.[2]

To address this need, many types of fire retardants have been developed and made available commercially; these include phosphorus- and halogen-based fire retardants and intumescent fire retardants (IFRs). Each type of fire retardant works in a unique way. For example, phosphorus-based compounds form a protective layer, either as a glassy surface barrier or by producing char, after exposure to fire. However, halogen- and antimony-based fire retardants are not preferred because both are toxic and ecologically unsafe.[3,4] On the other hand, another type of fire-retardant materials, known as *intumescent materials*, has gained wide acceptance in the world for fire protection.

IFR coatings are entirely different compared with phosphorous-, aluminum hydroxide, and organohalide-based fire retardants in terms of both mechanism and performance. Intumescent coatings expand upon exposure to fire and form a protective layer that is many times thicker than the original coating. Thus, the expanded char layer protects the substrate from the extreme heat of the fire.[5] Intumescent coatings have three main components: (1) an inorganic acid, typically ammonium polyphosphate (APP); (2) a carbon source, typically pentaerythritol; and (3) a gas source, typically melamine. The protective mechanism

**Table I.** Weight Percentage of the IFR Coating

| No. | EG | APP | Melamine (Mel) | Boric acid | Epoxy | ACR hardener |
|-----|-----|-------|----------------|------------|-------|--------------|
| C1 | | 11.76 | 11.76 | | 51 | 25.48 |
| C2 | | 11.76 | | 11.76 | 51 | 25.48 |
| F1 | 5.88 | 11.76 | 11.76 | — | 47.08 | 23.52 |
| F2 | 5.88 | 11.76 | — | 11.76 | 47.05 | 23.52 |
| F3 | 5.55 | 11.76 | 11.11 | 5.55 | 44.02 | 22.01 |
| F4 | 5.55 | 11.76 | 8.33 | 8.33 | 44.02 | 22.01 |
| F5 | 5.55 | 11.76 | 5.55 | 11.11 | 44.02 | 22.01 |

of an intumescent coating depends on the selection of its components and the suitability of the combinations. Intumescent coatings are also called *passive fireproofing materials*.[6,7] When an intumescent coating is subjected to heat, the surface begins to melt into a highly viscous liquid, and a series of chemical reactions start to occur, which produce inert gases. Because of the presence of the viscous liquid, the inert gases are prevented from escaping and remained trapped inside the gummy liquid. This results in expansion of the coating, usually up to many times its original thickness, to form a shielding carbonaceous char, which acts as an insulative barrier between the fire and the substrate.[8] The char expansion of the intumescent coating depends significantly on the ratio of carbon, nitrogen, and phosphorus atoms in the compound.[9] The formation of an intensifying carbonaceous charred layer is the fundamental requirement of an intumescent system. It is generally achieved by the addition of blowing agents, such as urea, urea–formaldehyde resins, polyamides, and melamine.[10]

In this research, we studied the effect of boric acid and melamine at different concentrations (weight percentages) in intumescent coating compositions. The coatings were composed of expandable graphite (EG) as the carbon source, APP as the acid source, melamine as the gas source, boric acid as the acid source, and bisphenol A epoxy resin BE-188 (BPA) with ACR hardener H-2310 polyamide amine as the binder.

## EXPERIMENTAL

Graphite flakes, melamine, and boric acid were purchased from Sigma-Aldrich (M) Sdn. Bhd. (Malaysia). APP was provided by Clariant (Malaysia) Sdn. Bhd. Acetic acid, sulfuric acid, $KMnO_4$, BPA, and ACR hardener H-2310 polyamide amine were purchased from Mc-Growth Chemical Sdn. Bhd. (Malaysia). The structural steel A36M was supplied by TSA Industries (Ipoh) Sdn. Bhd. Malaysia.

### Preparation of the Coating Mixture and Coated Steel Substrate

EG was prepared by the reaction of the graphite flakes with acetic acid, sulfuric acid, and potassium permanganate at a ratio of 1 : 2 : 0.5 : 0.07.[11] All intumescent ingredients were mixed according to their respective weight percentages, as indicated in Table I. A shear mixer was used to mix the coating ingredients at 40 rpm for 30 min. A structural steel plate measuring 100 $cm^2$ was used as the substrate. The coating was applied evenly onto the steel substrate with a brush. The coating thickness was

ensured at 1.5 mm by measurement with a digital vernier caliper. Seven formulations were prepared, and the coated substrate was cured in an oven at 60°C for 1 h.

### Analysis and Characterization

**Heat Shielding Effect.** Fire testing was conducted for each formulation to evaluate the penetration of heat from the fire to the steel substrate. The setup for the fire test is shown in Figure 1. The test was carried out for 60 min. A portable Bunsen burner was used to burn the coating, and the distance between the coating and the Bunsen burner was set at 7 cm. Three thermocouples, type K, were connected to an Anarittsu Data logger (input channel 6, model AM-8000K with Anarittsu software), whereas the other end of each thermocouple was connected to the uncoated surface of the substrate. The temperature of the uncoated (backside) surface of the steel plate was measured for 60 min at intervals of 1 min.

**X-Ray Diffraction (XRD, Bruker D8 advance Diffracto meter, Bruker Germany).** The residual char composition of the intumescent coating was analyzed by XRD measurements performed on Bruker AXS D8 Advance diffractometer with Cu Kα radiation and a nickel filter ($k = 0.150595$ nm, $k$ is wavelength of absorption edge of Nickel) in the range $10° < 2\theta < 90°$.

**Scanning Electron Microscopy (SEM).** The char layers and their morphological structures were observed and analyzed with an AMARY 1000 SEM instrument.

**Fourier Transform Infrared (FTIR) Spectroscopy.** The residual char composition was analyzed by a Shimadzu FTIR spectrometer in the range 4000–400 $cm^{-1}$.

**Thermogravimetric Analysis (TGA).** TGA of the intumescent coating samples (ca. 10 mg) was carried out at 10°C/min under $N_2$ over the whole temperature range 50–830°C by a TGA Q50 instrument.

## RESULTS AND DISCUSSION

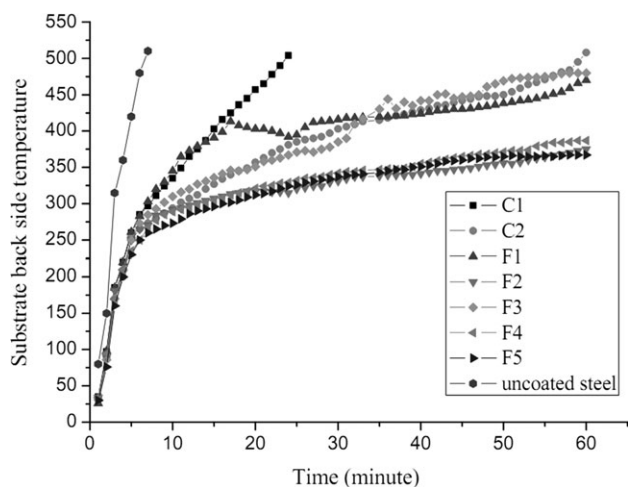### Heat Shielding Effect and Char Expansion

In this research, seven coating samples with different compositions of intumescent ingredients were prepared. The flame temperature of the Bunsen burner was 954°C. Figure 2 shows the temperature of the backside of the coated steel substrate versus time (in minutes), and Figure 3 shows the expansion of the char after fire testing. Figure 4(a–f) shows the physical appearance of formulations C2, F1, F2, F3, F4, and F5 after fire testing.

**Figure 1.** Fire test setup for the heat insulation test of the intumescent formulation: (a) portable Bunsen burner, (b) stand, and (c) sample of intumescent coating.

As shown in Figure 2, the uncoated steel substrate could only sustain its integrity for about 9 min after the fire had started; after that, the temperature started to rise above 500°C. For the C1 coating, the backside temperature of the steel substrate was 504°C after 24 min. During the fire, the C1 char was completely detached from the steel substrate without leaving any reaction product on the surface of the steel substrate to protect it from fire. The C1 coating contained APP, melamine, epoxy, and hardener. The detachment of the C1 char was possibly due to the decomposition of melamine phosphate, a product that was formed as the result of the reaction between APP and melamine. When the substrate temperature reached above 350°C, the melamine phosphate started to decompose and detached itself from the steel substrate. Formulation C2 showed better results than C1, where temperatures at the backside of the substrate after 30 and 60 min were 403 and 508°C, respectively. The C2 char cracked but remained attached to the substrate, as shown in Figure 4(a).

Coating F1 showed 1100% expansion of char as illustrated in Figure 2. This significant expansion was due to the presence of melamine, which functions as a blowing agent and is responsible for expanding the char. Initially, the formulation expanded uniformly, but after a certain time, it was oxidized and was no longer able to protect the steel substrate. In the flame area, the hole is formed, as shown in Figure 4(b). The backside temperatures of the steel substrate after 30 and 60 min were 416 and 470°C, respectively, as indicated in Figure 2. The char structure of the F1 formulation, which contained EG, APP, melamine, and epoxy resin with hardener, could not be sustained at 952°C for 60 min because the formulation did not contain any ingredient that could enhance the mechanical resistance of the char.

The expansion of F2 was 300%; this was the lowest relative to the expansion of the other formulations. The backside temperature of the substrate was 331°C and was less than that of F1; even after 60 min, the backside temperature only reached 375°C. The F2 char after the fire test is shown in Figure 4(c), which shows that there was no crack and no holes in the char. The F2 composition was completely different from that of F1, and as mentioned earlier, the reaction mechanism was also different. F1 contained 11.76 wt % melamine and no boric acid, whereas F2 contained 11.76 wt % boric acid and no melamine.



**Figure 2.** Heat shielding effect temperature curve for various formulations.
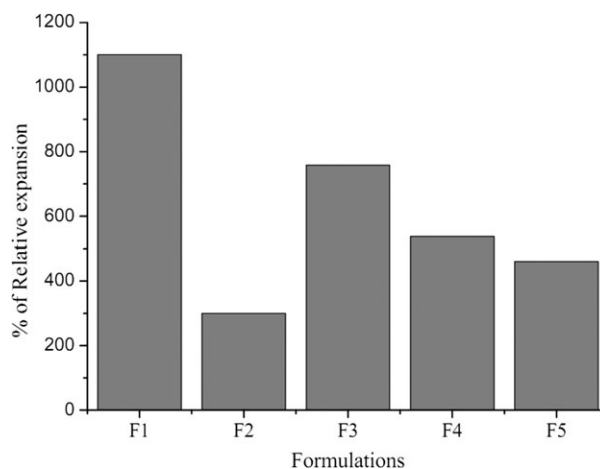


**Figure 3.** Relative expansion of the formulations.
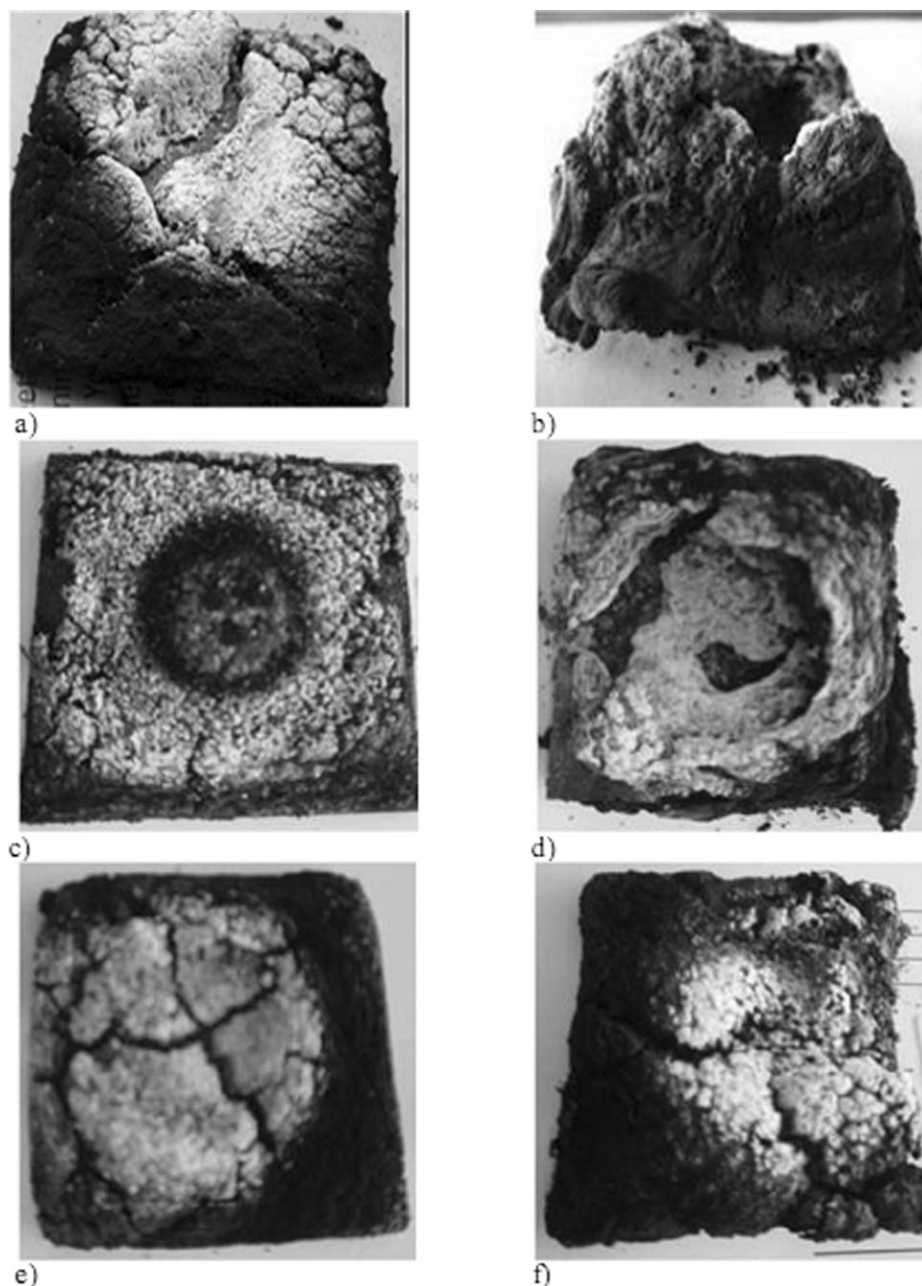
**Figure 4.** Photographs of char after fire test: (a) cracked char of C2, (b) F1 inside hole, (c) F2 thick char, (d) F3 crack and holes due to the oxidation of char, (e) F4 cracked surface of the char, and (f) F5 small cracks on the surface.

The absence of melamine, a blowing agent, reduced the expansion of the F2 formulation compared to the F1 formulation. However, the F2 formulation was well bonded to the substrate. The observation for the F2 formulation could have been because of the reaction between boric acid and APP, which formed borophosphate and boron oxide, which were the final protective layers on the substrate.[6]

The char of formulation F3 after the fire test is shown in Figure 4(d); holes and cracks were observed in the char. The backside temperature of the substrate after 30 min was 385°C, and after 60 min, the temperature reached 480°C. This was higher by 2.1

and 28% compared to F1 and F2, respectively, after 60 min. The F3 was formulated by the combination of melamine and boric acid with other intumescent ingredients. The expansion of F3 was 758%; this was 158% higher than F2 but was 45% lower than F1. The presence of melamine in the F3 intumescent coating expanded the char, and boric acid provided the resistance with the formation of borophosphate and boron oxide, which formed the protective layer on the steel substrate. However, the char did not protect the substrate because of cracks, as shown in Figure 4(d). The presence of cracks was due to the lower percentage of boric acid used in the formulation, which was 5.5 wt % of the total composition.
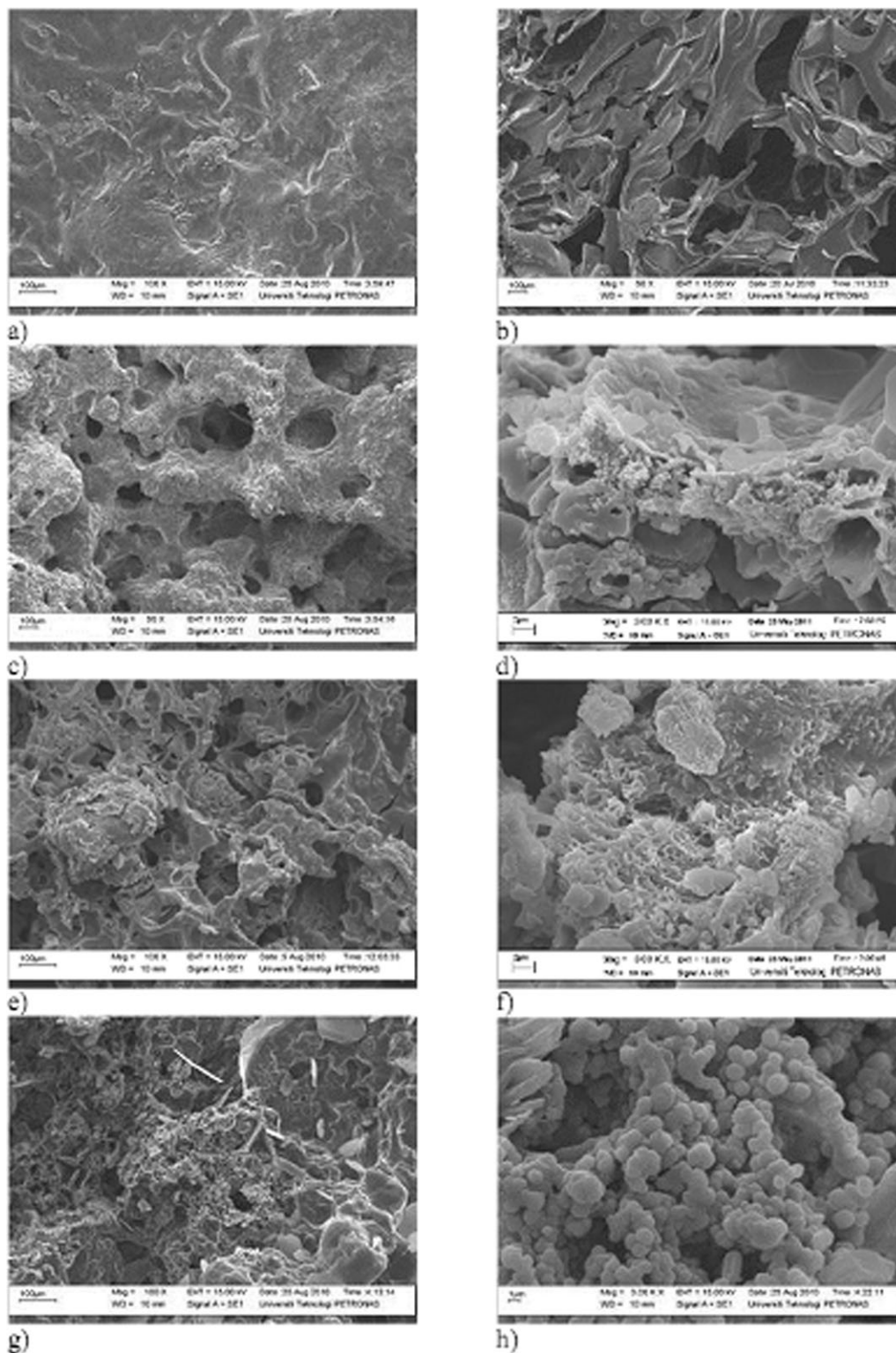
**Figure 5.** Char morphology of intumescent coating formulations: (a) F1 outer surface, (b) F1 cracked inner surface, (c) F2 inner surface with thick porous char layers, (d) F2 cracked char, (e) F4 inner surface thick porous and cracks, (f) F4 thick char surface, (g) F5 thick inner surface, and (h) F5 high magnification showing agglomerates.

The condition of F4 char after the fire test is shown in Figure 4(e). The expansion of F4 was 537%; this was 104%, 41% lower than F1 and F3 but 79% higher than F2. The expansion of F4

char was attributed to the presence of melamine, as shown in Figure 3. The backside temperatures of the F4 coated steel substrate after 30 and 60 min were 342 and 387°C, respectively;
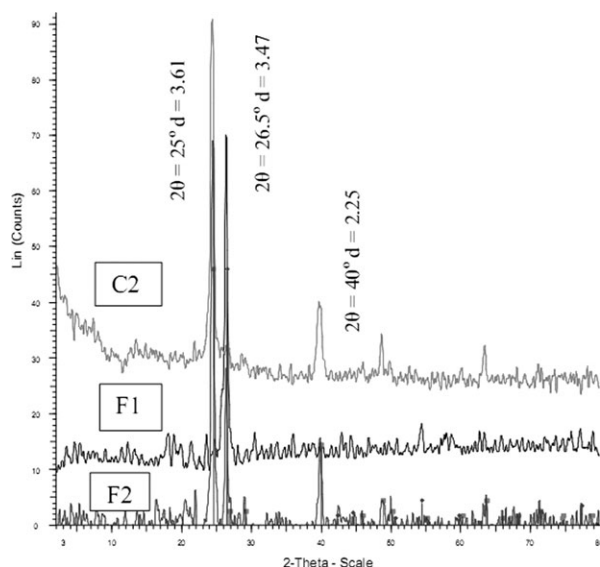
**Figure 6.** XRD spectra of the intumescent formulations.

this was 24% lower than F1 and 21% lower than F3 but 3.2% higher than F2. Increasing the amount of boric acid from 5.55 to 8.33% in F4 resulted in a decrease in the expansion, whereas the heat shielding effect of the formulation was increased. As shown in Figure 4(e), cracks appeared on the surface of the coating formulation with the sticky char attached onto the substrate. Because of the cracks, the backside temperature of the substrate gradually increased after 60 min.

Figure 4(f) shows F5 char after the fire test. Very small cracks could be observed on the surface of the char, and it was also observed that the char did not expand as much as the F1, F2, F3, and F4 formulations. The backside temperatures of the F5 coated steel substrate after 30 and 60 min were 337 and 367°C, respectively. The recorded temperature after 60 min was 28% less than F1, 2.1% less than F2, 30% less than F3, and 5.4% less than F4. The F5 formulation contained 11.11 wt % boric acid. On the basis of the composition, it was most likely that the char expansion of F5 was hindered by the high concentration of boric acid in the formulation. However, the adhesion of char to the substrate was increased. It was reported in the literature that when APP and boric acid were combined with resin, the backside temperature of the steel substrate reached 400°C in 29.5 min compared to 4 min for epoxy resin alone, and char remained well stuck on the substrate.[12]

### SEM

The SEM micrograph of chars from the four coating formulations, F1, F2, F4, and F5, are shown in Figure 5(a–h).

Figure 5(a) shows the outer surface of F1 char, and Figure 5(b) shows the inner surface. From the figure, the outer surface was observed to have a smooth texture, whereas cracks and holes were observed at the inner surface of the char, which was a very thin layer. The presence of cracks and holes explained the results of the heat shielding effect, where the backside temperature increased to 470°C after 60 min. Figure 5(c,d) shows the morphology of F2; the inner surface was very thick and porous with

holes, which were produced as a result of the dehydration of the coating during fire testing. The thick char layer reduced heat penetration in the steel substrate; the recorded backside temperature was 375°C. Figure 5(e,f) shows the char structure of the F4 formulation. It was observed that F4 had the same structure as F2, but there were cracks on the inner surface of F4, which accounted for the increase in the backside temperature of the F4 coating during the fire test. The char morphologies of the F5 formulation are presented in Figure 5(g,h). The inner surface of the char was thick and porous because of bubbles and agglomerates, which were formed because of the emission of $CO_2$ and $NH_3$ gases during the fire test. The emitted $N_2$, $NH_3$, and $CO_2$ bubbled through the viscous liquid and expanded the char. This explained the thirst of APP, boric acid, EG, and melamine with cured epoxy resin proceeded in the range of their apt temperature with the formulation with $N_2$, $NH_3$, $CO_2$, borophosphate, and boron oxide. The char layers of the intumescent formulation with bubbles acted as a fire-resistant layer provided heat insulation and, thus, shielded the steel substrate.

The multiporous arrangement of char can hinder heat relocation to the substrate and insulate the base substrate from the adverse effects of heat. The relocation rate of heat through the charring layers depends on the expansion and structure of the residual char. The expansion and structure of the char are very vital to common fire-retardant properties of coatings.[13]

### XRD

When the char layer continued to be oxidized at high temperatures, the carbon and inorganic materials originally present in the intumescent formulation barely remained in the carbonous char. However, the presence of inorganic materials in char is important, as they provide shielding in the later stages of fire, when the temperature is higher than 600°C.[14] The facial residue char of samples C2, F1, F2, F3, F4, and F5 tested at 800°C were
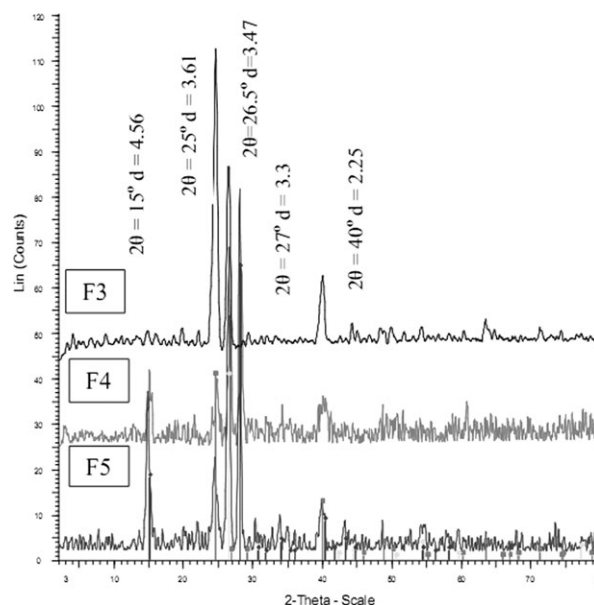


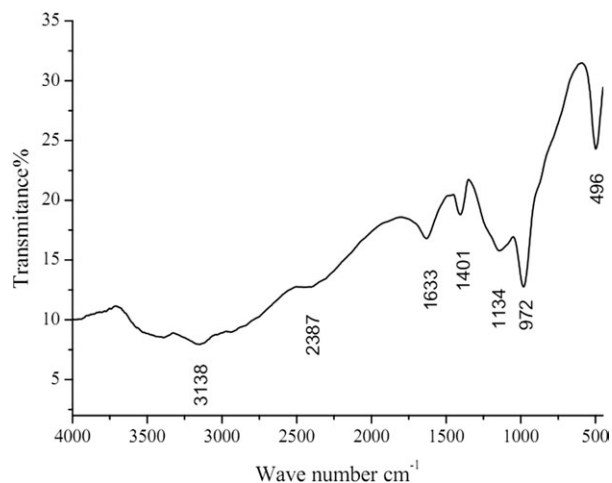**Figure 7.** XRD spectra of the intumescent formulations.

**Figure 8.** FTIR spectra of formulation F1.

analyzed by XRD; the spectra are shown in Figures 6 and 7. Figure 6 shows a comparison of the XRD analyses of C2, F1, and F2. C2 showed two peaks at $2\theta = 25$ and 40 with $d$ (the interplaner spacing) $= 3.61$ and 2.25, respectively, and identified as borophosphate (JCPDS card no. 34-0132) and boron oxide (JCPDS card no. 06-0297), respectively. These were recognized as contributing to good fire-retardant properties.[12] F1 showed one peak at $2\theta = 26.5°$ and $d = 3.47$, which was assigned to graphite (JCPDS card no. 12-0212), which also helped to reduce the effect of fire. For F2, three peaks were observed. The first peak at $2\theta = 25$ and $d = 3.61$ was borophosphate, the second peak at $2\theta = 26.5°$ and $d = 3.47$ was graphite, and the last peak at $2\theta = 40°$ and $d = 2.25$ was assigned to boron oxide. The presence of these compounds in the residual char was considered helpful in minimizing heat flow to the substrate.

Figure 7 shows the XRD spectra of the F3, F4, and F5 char residues. F3 showed three peaks: the peak at $2\theta = 25°$ and $d = 3.61$ was borophosphate, the peak at $2\theta = 26.5°$ and $d = 3.47$ was graphite, and the last peak at $2\theta = 40°$ and $d = 2.25$ was boron oxide. These peaks were identical to the peaks found for F2.

The char residue of F4 and F5 were found to have five similar peaks at $2\theta = 15, 25, 26.5, 27,$ and $40°$ and $d = 4.56, 3.61, 3.47, 3.3,$ and 2.25; these corresponded to boron oxide, borophosphate, graphite, sassolite, and boron oxide, respectively. The formation of sassolite (mineral acid of boric acid, $H_3BO_3$) has been shown to support the formation of $B_2O_3$, a glasslike material that increases the viscosity and prevents the gaseous decomposition products from evading the char to feed the flame.[12] F3 did not show the presence of sassolite, possibly because it contained less than 5.5 wt % boric acid, compared to the F4 and F5 coatings, which contained 5.5 wt %. The XRD results showed that the reaction between boric acid and melamine, APP, and $O_2$ enhanced the antioxidation performance of the intumescent coating by the formation of a protective char layer on the steel substrate. The XRD results also showed that boric acid in the char was converted into boron oxide and sassolite. In turn, the boron oxide reacted with APP to form borophosphate, which is a very stable compound up to 1200°C.[15] However, melamine or its derivate could not be detected from

the XRD spectra; this could be explained as due to the reaction between melamine and APP to form melamine phosphate, which decomposed at temperatures above 350°C. Because the char was produced at 800°C, the melamine probably decomposed completely.

**FTIR Analysis**

FTIR spectra were recorded with a Shimadzu spectrometer in the range 4000–400 cm$^{-1}$ with an ATR system. This range was selected to analyze the residual component in the char. Char samples were ground, and 50 scans were run to obtain spectra with a fine signal-to-noise ratio. The char residues were analyzed with spectroscopic tools to understand the mechanism of interaction among EG, APP, melamine, boric acid, epoxy, and the hardener. The FTIR spectra of the F1, F2, F4, and F5 formulations are shown in Figures 8–11. The FTIR spectrum of F1 in Figure 8 represents the phosphate and melamine region. In the region of phosphate (P—O—P) between 1400 and 800 cm$^{-1}$, phosphate ($PO_4^-$) was detected at 1140 cm$^{-1}$. The carbonyl stretching of $CH_2$ or $CH_3$ occurred at 1402 cm$^{-1}$, with three weak bands of amino groups (C—N = 31,622, C=N = 2440, and C≡N = 1621 cm$^{-1}$). In the region 1380–1700 cm$^{-1}$, three peaks were detected at 1619, 1521, and 1429 cm$^{-1}$ which were due to amino groups ($NH_2$) and to a ring (C, N).[16] Figure 9 shows the region of borate and phosphate; B—O—P bending motion was detected at 624 cm$^{-1}$, and O—P—O in borophosphate appeared at around 588–545 cm$^{-1}$. The peak at 541 cm$^{-1}$ in $B_2O_3$ was assigned to the $\delta$(O—B—O) mode.[17] In the region of P—O—P from 1400 to 800 cm$^{-1}$, the peak at 924 cm$^{-1}$ was due to P—O asymmetric vibrations in the P—O—P chain, whereas the symmetric vibration was present at 1088 cm$^{-1}$. In the 1380–1700-cm$^{-1}$ region, the peak at 1591 cm$^{-1}$ was due to amino groups ($NH_2$), and that at 1454 cm$^{-1}$ was due to a ring (C, N).[16] The presence of these groups were due to the decomposition of APP and the polyamide hardener.

The spectra of F4 and F5, shown in Figures 10 and 11, respectively, showed identical peaks because they contained the same ingredients and were tested in the same fire test environment. The only difference between F4 and F5 was the amount (weight percentage) of melamine and boric acid. In the P—O—P region
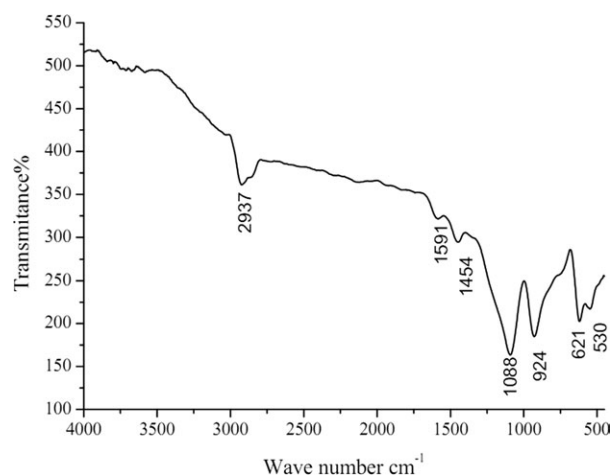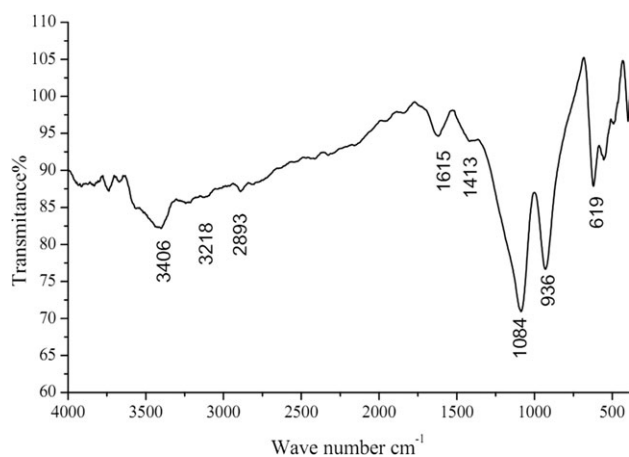


**Figure 9.** FTIR spectra of formulation F2.

**Figure 10.** FTIR spectra of formulation F4.



**Figure 12.** TGA of C1, C2, F1, F2, F4, and F5.

from 1400 to 800 cm$^{-1}$, P—O asymmetric vibrations in the P—O—P chain were detected at 906 cm$^{-1}$, whereas the symmetric vibrations were at 1084 cm$^{-1}$. The asymmetric vibrations of the P—O group occurred in the region 890–950 cm$^{-1}$, and the P—O symmetric region of the P—O—P chain was at 1400–1080 cm$^{-1}$.[18,19]

In the second region from 1380 to 1700 cm$^{-1}$, the two peaks at 1413 and 1615 cm$^{-1}$ represented the stretching vibrations of CH$_2$ or CH$_3$ deformation vibrations and polyaromatic compounds, respectively. In the third region above 2100 cm$^{-1}$, there were two weak bending peaks at 2833 and 3467 cm$^{-1}$; these represented the bending vibrations of —CH$_3$—CH$_2$— and O—H groups. The results suggest that the thermal degradation of the coating formulations occurred in two major phases; the first stage of degradation occurred in the 400–500°C range, and the second stage occurred at 600–700°C. As illustrated in Figure 8, the second stage led to the formation of a compact char with the absorption of polyaromatic and phosphorous compounds, with boron phosphate and boron phosphate oxide as the main components of char at 800°C. These results were in good agreement with those of the XRD analysis.
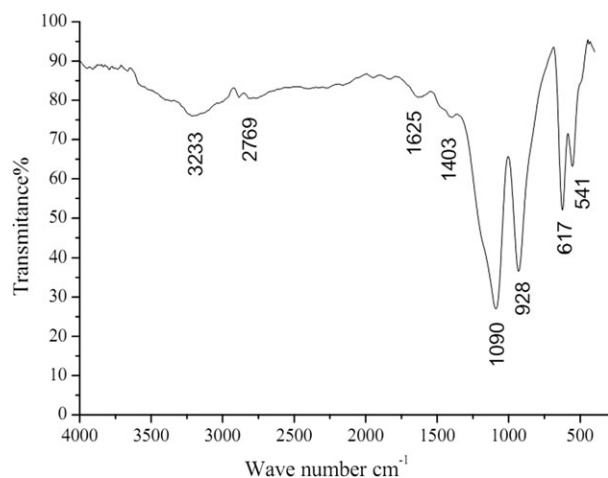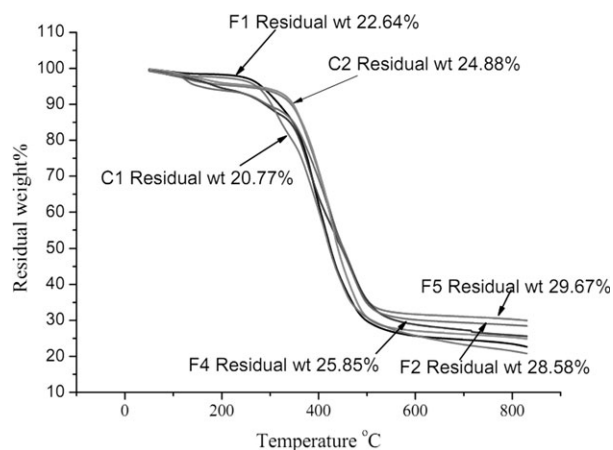
## TGA

The degradations of boric acid and melamine have been reported in the literature.[20,21] The degradation of boric acid is a two-step mechanism. The first step of degradation occurs between 100 and 140°C and results in about a 30% weight loss, and in the second step, which occurred in the temperature range 140–200°C, which is the most important range in producing a thermally stable material, further weight loss occurred, amounting to 55 wt % of the initial mass.[15]

The residual weights at 800°C of the C1, C2, F1, F2, F4, and F5 formulations obtained from TGA were 20.77, 24.88, 22.64, 28.58, 25.85, and 29.67%, respectively. The TGA curve of each formulation is illustrated in Figure 12. The residual weight of C2 was 19.7% higher than that of C1. The higher residual weight was attributed to the formation of borophosphate in the residual char of C2. A comparison of residual weight between F1 and F2 showed that F2 had a residual weight 26% higher than that of F1. Because both C2 and F2 contained boric acid and their other ingredients were the same, these results indicated that the boric acid formulations gave higher residual weights compared to the melamine formulations. The results of heat shielding, XRD, FTIR spectroscopy, and SEM analysis also
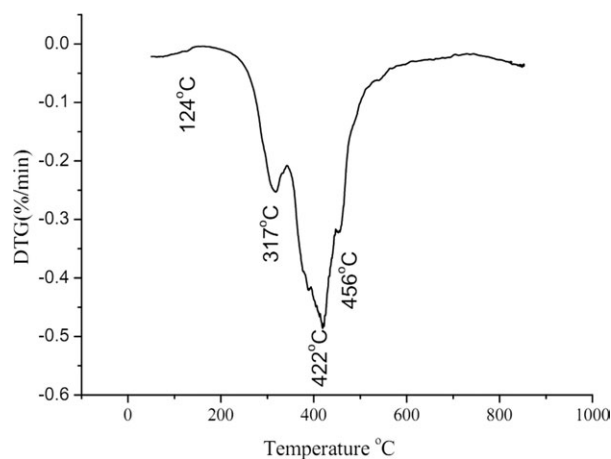


**Figure 11.** FTIR spectra of formulation F5.



**Figure 13.** Differential thermogram (DTG) curve of C1.
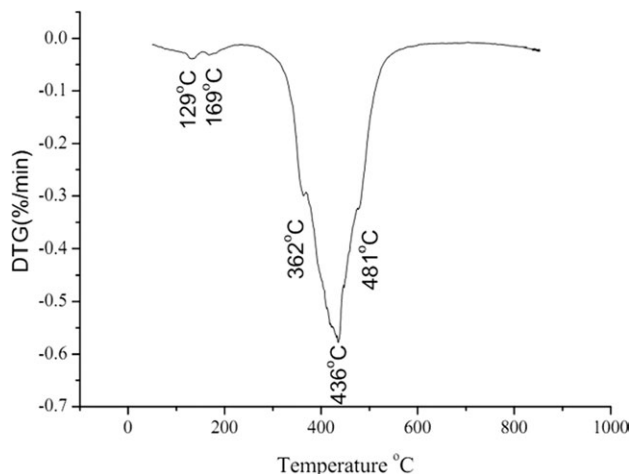
**Figure 14.** DTG curve of C2.



**Figure 16.** DTGA curve of F2.

showed that the boric acid formulations had better heat insulating performances than the melamine formulations. The formulation F4 had a lower residual weight percentage than formulation F5. as it contained a lower concentration of boric acid than did F5. These results suggested that the degradation/reaction products of boric acid were main the components in the final protective char that developed after the intumescent coating was exposed to fire.

The DTGA curve confirmed four steps of thermal degradations for C1, as shown in Figure 13. The first degradation, which occurred at 124°C, was due to the polyamide hardener. The second degradation, at 317°C, was due to the degradation of melamine and APP with the release of $N_2$ and $NH_3$. The third degradation, at 422°C, was due to the decomposition of epoxy, and the fourth degradation, at 456°C, was due to the decomposition of the polyamide hardener.

The DTGA curve of C2, illustrated in Figure 14, had five steps of thermal degradation at 129, 169, 362, 436, and 481°C. At 129°C, boric acid was converted into meta boric acid through dehydration, and at 169°C, the dehydration of meta boric acid produced boron oxide.[15] Although the decompositions of BPA
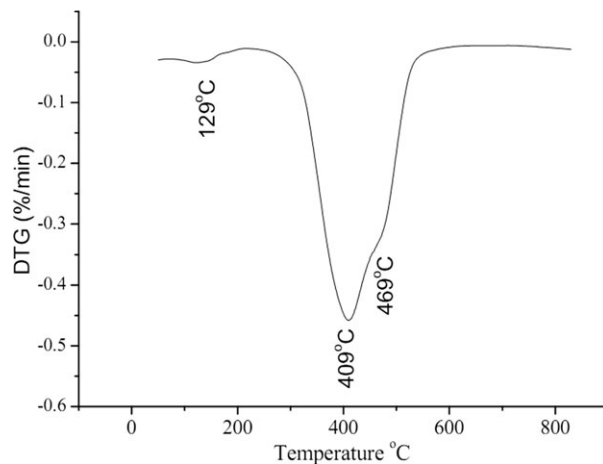
epoxy resin and APP were confirmed at 362 and 436°C, respectively, the degradation of polyamide hardener occurred at 481°C. The acid boric content in the C2 formulation caused the degradation temperature of each step to increase as boric acid reacted with APP to form borophosphate. At 450°C, only crystalline borophosphate and boron oxide glass remained. This indicated that borophosphate was obtained as the product of the reaction between the degradation products of boric acid and APP. That is, boron oxide and phosphoric acid reacted together to yield borophosphate.[22]

As shown in Figure 15, the degradation of the F1 melamine formulation occurred in two steps, at 289 and 400°C; these steps represented the decomposition of melamine and other intumescent ingredients, such as APP, EG, epoxy, and the hardener, respectively. Melamine started to decompose after 290°C, and a portion of the melamine reacted with APP to form melamine phosphate.[2] The melamine phosphate decomposed after 350°C.

The DTGA curve of F2, as illustrated in Figure 16, showed a three-step decomposition at 129, 409, and 469°C. The degradation at 129°C was due to boric acid. That at 409°C was due to the degradation of melamine phosphate, and that at 469°C was
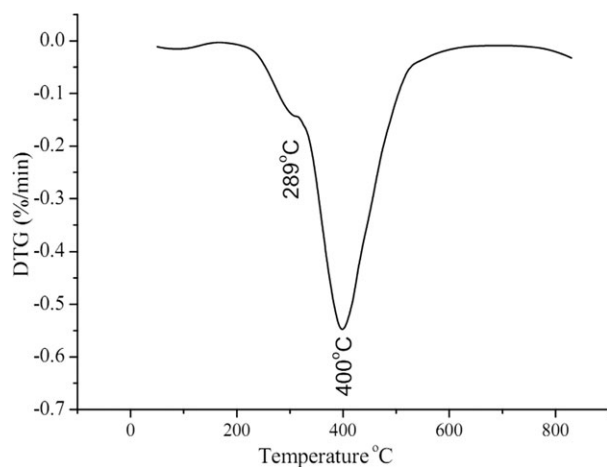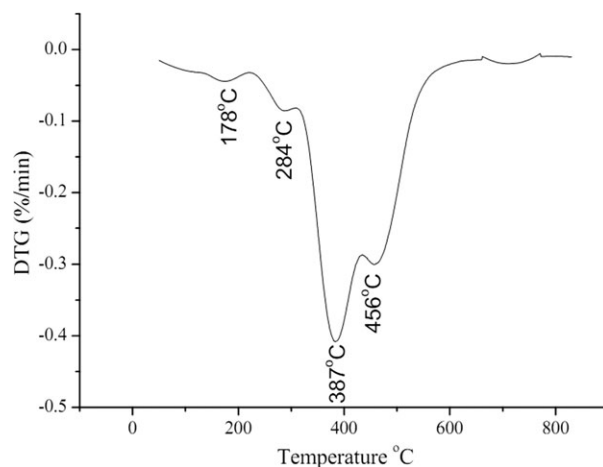


**Figure 15.** DTG curve of F1.
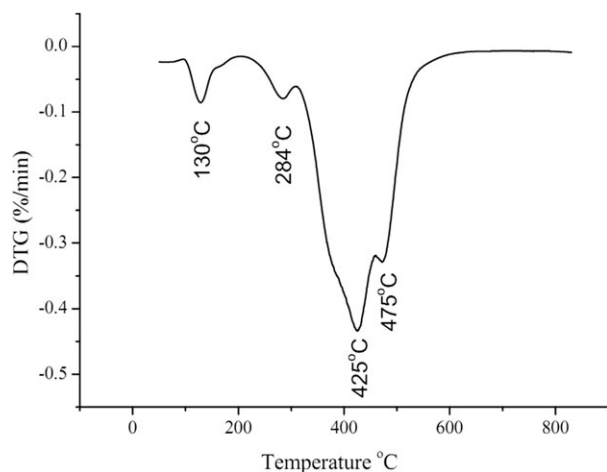


**Figure 17.** DTG curve of F4.

**Figure 18.** DTG curve of F5.

the degradation of boron phosphate due the chemical reaction product of the coating formulation. The F4 formulation was a combination of melamine and boric acid, which showed a four-step degradation. Also, the degradation of all of the intumescent ingredients occurred at different temperatures from those of other formulations. From Figure 17, the decomposition of boric acid into boron oxide occurred at 178°C, decomposition of melamine occurred at 284°C, the decompositions of EG and melamine phosphate occurred at 387°C, and the decomposition of the polyamide hardener occurred at 456°C. As the weight percentage of melamine in F4 was higher than that of boric acid, the variation in temperature derivation, especially at 387 and 456°C, were compared to the results reported in Figure 13–16. The TGA curve of F5 is shown in Figure 18. The decomposition of F5 started much earlier than those of the other formulations; the decomposition of boric acid started at 130°C, and the intermediate product of metaboric acid was further converted into boron oxide. The decomposition of melamine remained at 284°C, whereas the decomposition of melamine phosphate started at 425°C, and the decomposition of boron phosphate occurred at 475°C. The shift in decomposition temperature of the F5 formulation was attributed to the increased boric acid weight percentage with respective to melamine. The results of TGA and DTGA showed similar thermal degradation behavior for the F4 and F5 formulations, as both formulations contained the same intumescent materials. However, the percentage weight loss was different, as the weight percentages of melamine and boric acid in the formulations were different. Increasing the weight percentage of boric acid with respect to melamine contributed to the increased residual weight. Among all of the formulations, F5 recorded the highest residual weight percentage of 29.67%, which was higher than those of C1, C2, F1, F2, and F4 by 42, 19, 31, 3.8, and 12%, respectively. This showed that the F5 coating enhanced the intumescent effect in terms of the residual weight percentage of char compared to other formulations.

## CONCLUSIONS

The results of this study show that both melamine and boric acid contributed toward improving the heat insulation properties of the intumescent materials but each in its own way. On the basis of the results of the formulations containing melamine, we deduced that melamine acted as a blowing agent and helped to expand the carboneous char. The F1 coating showed a char expansion of 1100% when the backside substrate temperature was 470°C. On the basis of the results of the boric acid formulation, F2 showed a char expansion 300% when the substrate temperature was 375°C. These results show that the reaction products of melamine decomposed, whereas boric acid remained in the char and protected the substrate from fire. When the weight percentage of boric acid was increased with respect to melamine in the formulation, the fire protection performance was improved. F5 showed better results when the temperature of the backside of substrate was 367°C after 60 min. The effect of EG also helps to expand the carboneous char and increase the residual weight of the char, which was also helpful for minimizing the flow of heat to the substrate. The SEM results showed that the structure of the residual char became porous when the weight percentage of boric acid was increased with respect to that of melamine. XRD and FTIR spectroscopy showed the presence of graphite, borophosphate, sassolite, and boron oxide in the residual char. These compounds were helpful in reducing the temperature of the backside substrate plate because of their high thermal stability. TGA and DTGA showed that F5 (boric acid = 11.11wt %) enhanced the residual weight by 31% compared to that of the F1 coating (melamine = 11.76 wt %). The addition of 11.11 wt % of boric acid in F5 created an oxide-layer-like protective barrier on the surface of the insulating char. Thus, the flow of the heat was reduced to the substrate, and this reduced the backside substrate temperature.

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